UNCONJUGATED CHROMOPHORIC INTERACTIONS RELATED TO CYCLOPOLYMERIZATION

By

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CHAPTER I

INTRODUCTION

Chromophoric Interactions

The most typical chromophoric interaction is conjugation. The larger extent of electron delocalization that is possible as conjugation increases contributes toward stabilization of the excited state more than toward stabilization of the ground state. As seen from the basic relationship

$$E = \frac{hc}{\lambda}$$

a decrease in the energy difference between ground state and excited state will cause bathochromic shifts of λ_{max}. Polyenes, for example, give the ultraviolet absorptions shown in Table 1[1, 2 p. 228 ($\pi \rightarrow \pi^*$ transition).

TABLE 1

ULTRAVIOLET ABSORPTION OF POLYENES

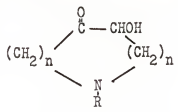
Alkene	λ_{max} (mμ)	E
Ethylene	171	15,530
Butadiene	217	21,000
Hexatriene	268	34,600
Octatetraene	304	-

However, chromophoric interactions are not limited to conjugated systems. Many examples of interacting non-conjugated chromophores have been reported.[3] Such interspatial interaction results in

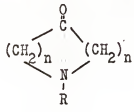
spectral effects which correspond neither to the simple addition of the spectra of the two insulated chromophores, nor to the spectrum of the completely conjugated system.[2, p. 437]

Braude[4] found strong ultraviolet absorption evidence for interaction between unconjugated unsaturated groups in systems of the type $X(CH_2)_nY$ (X and Y are chromophores); Bateman and Jeffrey[5, 6] showed by X-ray analysis that even for two single isolated chromophores some interaction occurred.

Leonard[7] observed interspatial ultraviolet nitrogen-carbonyl interaction in aza-acyloins (I) and aminoketones (II), caused by true bond or only partial orbital overlap of the lone pair of electrons on nitrogen with the $p\pi$ electrons of the carbonyl group. Result of the interaction was the decrease of the C=O peak (264 mμ) to a very weak absorption, and the appearance of a new strong band at 228 mμ.

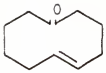


I



II

Leonard and Owens[8] observed a clear transannular double bond - carbonyl interaction in 5-cyclodecen-1-one (III). The spectrum obtained did not show additivity of the component parts IV and V; scale models showed that the carbonyl and the double bond could readily approach each other in parallel planes. The infrared spectrum and the dipole moment of III did not show any interactions; this prompted the authors to suggest that the interaction occurred only in the excited state.



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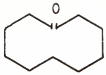

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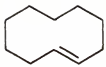


V

Winstein and Orloski[9, 10] prepared compounds containing structures VI and VII, which were fixed in a rigid boat conformation by adjoining rings. A comparison of the ultraviolet spectra of these compounds with the spectra of the corresponding saturated ketone VIII and mono-olefin IX showed the appearance of an additional peak, in a bathochromic position.

VI

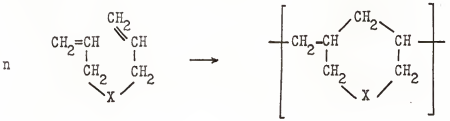
VII

VIII

IX

Cyclopolymerization

Intramolecular-intermolecular polymerization (commonly referred to as cyclopolymerization) is a phenomenon observed with many unconjugated dienes, by which a polymer having cyclic recurring units is formed.



This polymerization mechanism was first proposed by Butler and Angelo[11] in 1957, and was subsequently rigorously proved by

Butler, Crawshaw and Miller[12] through degradation studies of the polymers obtained from diallyl quaternary ammonium salts ($X = NR_2^+ Br^-$).

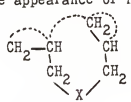
Since the establishment of the intra-intermolecular polymerization mechanism a large number of monomers have shown the ability to cyclopolymerize.[13] Cyclic units containing up to twenty-one carbon atoms have been observed;[14] heterocyclic rings where the central atom (X in the structures shown above) was oxygen, silicon, phosphorus, tin, or sulfur have been formed.[13]

The physical characteristic shared by all polymers obtained by intra-intermolecular mechanism is their solubility in organic solvents; this property indicates an absence of cross-linking.

Unconjugated Chromophoric Interactions Related to Cyclopolymerization

In an effort to account for the unique tendency of unconjugated diene systems to cyclopolymerize, Butler[3] suggested that a homoconjugative interaction may occur between the unconjugated ethylenic bonds. Such a phenomenon would have a stabilizing influence on the excited state of the molecule, thus providing an energetically favorable path from diene to cyclic product.

The various possible structures involved have been listed;[3] X is the most general. All these structures involve interspatial interactions, and as such their presence should be evident in ultraviolet spectra; their most common manifestations should be, as seen above, bathochromic shifts or the appearance of new peaks.



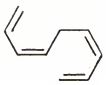
X

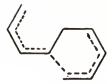
Butler and Brooks[15] studied the ultraviolet spectra of the cis and trans isomers of 1,3,8-nonatriene. The λ_{max} values for these two isomers were shifted bathochromically from the position which would be calculated by Woodward's[16] rule, namely 222 mμ (for both compounds), to 225.5 and 227 mμ respectively. trans-1,3,8-Nonatriene had been cyclopolymerized by the same authors.[15]

Butler and Raymond[17] synthesized 1,3,9,11-dodecatetraene, 1,3,6,8-nonatetraene and 3,6-dimethylene-1,7-octadiene, and the corresponding conjugated dienes 1,3-dodecadiene, 1,3-nonadiene, and 3-methylene-1-octene. The ultraviolet spectra of the compounds were studied. It was found that all of the dienes absorbed in the narrow range 224.7 - 226.5 mμ, while the tetraenes exhibited absorption maxima over the wide range of 221.8 - 272.1 mμ. The dodecatetraene and the nonatetraene showed bathochromic shifts of λ_{max} (2.7 and 10.6 mμ respectively) when compared with the corresponding dienes (nonadiene showed also two new absorption peaks). 3,6-Dimethylene-1,7-octadiene showed a hypsochromic shift of 2.9 mμ when compared with 3-methylene-1-octene.

The spectral data obtained were considered strong evidence of interactions present in the tetraenes. The hypsochromic shift of the octadiene derivative was explained with a larger ground state stabilization due to the several conformations available to the molecule where the two conjugated systems could approach each other.

All the tetraenes were cyclopolymerized,[18] and the authors postulated that the interactions observed in the ultraviolet spectra are the same ones which lead to a cyclic intra-intermolecular polymerization mechanism. For the nonatetraene, for example, the following structure was drawn.





Finally, van Heinigen[19] studied the ultraviolet spectra of 1,4-dimethylenecyclohexane (a compound known to cyclopolymerize[20]) and of methylenecyclohexane. It was found that the unconjugated diene showed both bathochromic shifts of λ_{max} and the appearance of new peaks when compared with the mono-olefin. The spectroscopic data are reported in Table 2.

TABLE 2

ULTRAVIOLET ABSORPTION OF METHYLENECYCLOHEXANES

Compound	95% Ethanol		Isoctane	
	λ_{max} (mμ)	E	λ_{max} (mμ)	E
Methylenecyclohexane	191.8	10,850	191.3	11,700
			197.5	9,200
1,4-Dimethylenecyclohexane	198.6	19,500	198.2	21,100
	203.3	17,200	202.8	18,500
	208.9	9,550	208.6	10,300

Statement of the Problem

The purpose of the present research was to prepare a series of unconjugated diene systems known to cyclopolymerize,[21-24] namely allyltrimethylsilane, diallyldimethylsilane, triallylmethylsilane, and tetraallylsilane, and study their ultraviolet spectra in an effort to determine whether nonconjugated chromophoric interactions occurred. A bathochromic shift of 2.4 mμ was observed between the monoallyl compound

and the diallyl compound, indicating an interaction in the diallyl compound. The total bathochromic shift between the monoallyl compound and the tetraallyl compound was 3.9 mμ, indicating some additional interaction as the number of allyl groups is increased.

It was determined to investigate the number of factors which could have caused these interactions by preparing series of related compounds and examining them in the ultraviolet region. Three main groups of compounds were prepared and studied: the vinyl analogues (trimethylvinylsilane, dimethyldivinylsilane, methyltrivinylsilane, and tetravinylsilane); the propyl analogues (allyltripropylsilane, diallyldipropylsilane, and triallylpropylsilane); the carbon analogues (3,3-dimethyl-1-butene, 3,3-dimethyl-1,4-pentadiene, 4,4-dimethyl-1-pentene, and 4,4-dimethyl-1,6-heptadiene). A compound of related interest, allyldimethylvinylsilane, was also studied.

CHAPTER II

RESULTS AND DISCUSSION OF THE ALLYLMETHYLSILANES STUDY

Isooctane Solutions

The ultraviolet absorption of isooctane solutions of allyltrimethylsilane (A1), diallyldimethylsilane (A2), triallylmethylsilane (A3), and tetraallylsilane (A4) (all known compounds) was determined. The values obtained are shown in Tables 3 and 4. All the compounds absorbed in the 190 - 200 mu region, with extinction coefficients ranging from 10,000 to 40,000.

Absorbance was plotted *vs.* path length for three different path lengths to check the adherence to Lambert's law (Figure 1); good adherence was obtained. Absorbance was plotted *vs.* molarity for four concentrations to check the adherence to Beer's law (Figure 2); fairly good adherence was obtained; a very slight deviation towards lower absorbance with increasing concentration was observed for the most concentrated solution. No obvious reason for this slight deviation was apparent; a mechanical error could possibly have been involved.

The λ_{max} values obtained for each of the four allylsilanes remained nearly constant when concentration or path length were varied. The very small variations observed (within $\pm$ 0.3%, see Table 2) did not seem to follow a trend (with respect to concentration or other variables) and were most likely due to reading error (wide absorption bands were obtained) or mechanical error (at the low wavelengths used higher slit

TABLE 3

λ_{max} AVERAGES OF ALLYLMETHYLSILANES (ISOOCTANE SOLUTIONS)

Compound	λ_{max} Average (mμ)	Departures from Average	Shift Average (mμ)	Shift Additivity (A2-A1 shift set at 1)
A1	192.3	± 0.3%	2.4	1.00
A2	194.7	± 0.1%	1.0	0.42
A3	195.7	± 0.3%	0.5	0.21
A4	196.2	± 0.3%		

TABLE 4

EXTINCTION COEFFICIENT AVERAGES OF ALLYLMETHYLSILANES (ISOOCTANE SOLUTIONS)

Compound	E Average	Departures from Average	Additivity (E_{A1} set at 1)
A1	10,566	± 6%	1.0
A2	19,190	± 4%	1.8
A3	28,840	± 7%	2.7
A4	37,271	± 6%	3.5

apertures are needed to provide sufficient energy, with consequent loss in reproducibility). However, at least four sets of values were obtained for every compound, so that the average value calculated would be significant; furthermore, even when variations in absolute wavelength were observed, the relative shift values remained constant within the various A1 - A4 series.

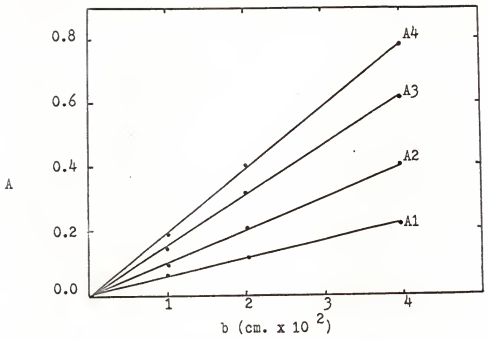


Figure 1.—Adherence to Lambert's law of allylmethylsilanes (isooctane solutions).

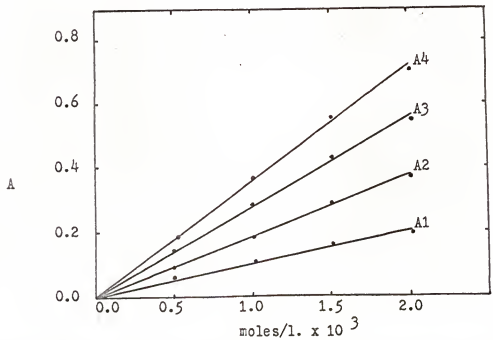


Figure 2.—Adherence to Beer's law of allylmethylsilanes (isooctane solutions).

The extinction coefficients obtained for each of the four allylsilanes remained fairly constant when the concentration or path length were varied, but not as constant as the λ_{max} values. Variations up to $\pm$ 7 per cent (see Table 4) were observed; again, the variations did not seem to follow a trend.

Table 3 shows how, with increasing allyl substitution in the silanes, the λ_{max} values shifted progressively towards longer wavelengths, with a total bathochromic shift of A4 over A1 of 3.9 mμ. This corresponds to an energy lowering of 2.96 kcal./mole in the $\pi \rightarrow \pi^*$ transition. The average shift lengths for the A2-A1, A3-A2, and A4-A3 shifts were 2.4, 1.0 and 0.5 mμ, corresponding to a 1.00/0.42/0.21 ratio (an asymptotic decrease in shift length).

Table 4 shows how, with increasing allyl substitution in the silanes, the extinction coefficient increased, but remained below straight additivity. The ratios were 1.0/1.8/2.7/3.5, showing that in nearly every case the extinction coefficients were 10 per cent short of additivity.

Summarizing the results obtained, the ultraviolet study of the four allylsilanes in isooctane solution showed that, increasing the degree of allyl substitution:

(i) a bathochromic shift occurs
(ii) the bathochromic shifts decrease asymptotically
(iii) the extinction coefficients increase progressively, but remain 10 per cent short of straight additivity.

Ethanol Solutions

Ninety-five per cent ethanol was chosen as polar solvent to be compared with the nonpolar isooctane only after the transmittance of the two solvents in the far ultraviolet was determined. The values obtained,

reported in Table 5, show that their transmittance in the region considered is very close.

TABLE 5

TRANSMITTANCE[a] OF ISOOCTANE AND 95 PER CENT ETHANOL IN THE FAR ULTRAVIOLET

Wavelength (mμ)	Isooctane	95 Per Cent Ethanol
200	98	94
195	82	88
190	72	72
185	43	31

[a]Solvent vs. nitrogen; path length 0.03 mm. Values are per cent transmission.

The spectroscopic data obtained for the ethanol solutions of the allylmethylsilanes (Tables 6 and 7) parallel the results obtained for the osooctane solutions. Absorbance was plotted vs. molarity for four concentrations to check the adherence to Beer's law (Figure 3); good adherence was obtained. All the λ_{max} values obtained for the ethanol solutions of the allylsilanes showed bathochromic shifts over the corresponding isooctane solutions.

Except for A1, which was shifted 1.3 mμ, the change in solvent from isooctane to ethanol caused a constant bathochromic shift of 0.8 mμ. As a consequence of the larger solvent effect for A1, the A2-A1 shift was smaller than the one observed with isooctane solutions (1.9 instead of 2.4 mμ), while the A3-A2 and A4-A3 shifts remained unchanged at 1.0 and 0.5 mμ. The total bathochromic shift of A4 over A1 was therefore reduced to 3.4 mμ. The shift ratios were now 1.00/0.53/0.26,

TABLE 6

λ_{max} AVERAGES OF ALLYLMETHYLSILANES (ETHANOL SOLUTIONS)

Compound	λ_{max} Average (mμ)	Departures from Average	Shift Average (mμ)	Shift Additivity (A2-A1 shift set at 1)
A1	193.6	± 0.2%	1.9	1.00
A2	195.5	± 0.1%	1.0	0.53
A3	196.5	± 0.1%	0.5	0.26
A4	197.0	± 0.1%		

TABLE 7

EXTINCTION COEFFICIENT AVERAGES OF ALLYLMETHYLSILANES (ETHANOL SOLUTIONS)

Compound	E Average	Departures from Average	Additivity (E_{A1} set at 1)
A1	9,150	± 8%	1.0
A2	18,715	± 2%	2.0
A3	27,616	± 3%	3.0
A4	35,954	± 2%	3.9

still close to an asymptotic decrease in shift length with increasing allyl substitution.

All the extinction coefficients obtained for the ethanol solutions showed hypochromic effects over the corresponding isooctane solutions. The average decrease in extinction coefficient of each compound was:

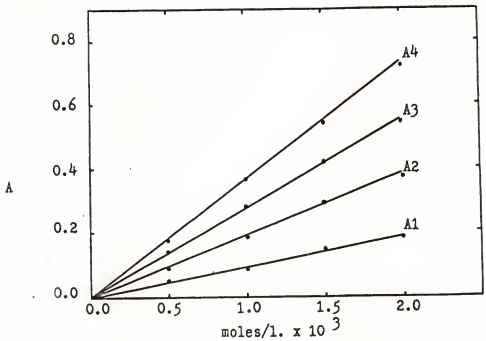


Figure 3.—Adherence to Beer's law of allylmethylsilanes (ethanol solutions).

A1	10.8%
A2	1.7%
A3	1.3%
A4	3.8%

It is seen that a marked decrease was observed only for A1. As a consequence of the pronounced decrease in intensity of A1, the extinction coefficient ratios for the ethanol solutions showed an almost exact additivity with increasing allyl substitution: 1.0/2.0/3.0/3.9.

Summarizing the results obtained, the ultraviolet study of the four allylsilanes in ethanol solution showed that, with a change in solvent from isooctane to 95 per cent ethanol:

(i) a bathochromic shift occurs for all the allyl compounds.
(ii) a hypochromic effect occurs for all the allyl compounds.
(iii) both bathochromic shift and hypochromic effect are more pronounced for allyltrimethylsilane than for the other allylsilanes.

Gas Phase

The low vapor pressure of the allylsilanes allowed only a qualitative study (determination of λ_{max} but not of the extinction coefficients) of the first three compounds in the allylmethylsilane series.

Similarly to the solution spectra, wide absorption bands were obtained. The spectroscopic data are reported in Table 8. All the compounds absorbed at a lower wavelength in the gas phase than in solution. The shifts observed are smaller than the ones obtained from solution spectra, but the shift ratios are identical.

TABLE 8

ABSORPTION OF ALLYLMETHYLSILANES IN THE GAS PHASE

Compound	λ_{max} (mμ)	Shift (mμ)	Shift Additivity (A2-A1 shift set at 1)
A1	188.7		
		1.0	1.0
A2	189.7		
		0.4	0.4
A3	190.1		

Comparison of the Different Media

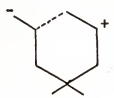
Phase and solvent effects in organic spectra can be interpreted at least qualitatively in terms of dipole, polarization, and hydrogen bonding forces between solute and solvent.[25] A treatment by Bayliss[2], p. 190 of polarization forces predicts bathocromic shifts in going (i) from gas phase to solution in non-polar solvents; (ii) from solution in nonpolar solvents to solution in polar solvents.

A comparison of the λ_{max} values for the methylallylsilanes obtained in gas phase, isooctane solution, and 95 per cent ethanol solution, shows a progressive bathochromic shift, as expected from the increase in polarization forces. According to Bayliss and McRae[25] the gas - solvent red shift is caused by a momentary polarization induced in the solvent by the transition dipole of the solute, and is more important when the solute is nonpolar. The fact that the shifts obtained in the gas phase were smaller than the ones obtained in solution could possibly be due to a higher energy state of the molecules in the gas phase,[2, p. 533] with consequent higher rotational and vibrational motions, hindering intramolecular interactions.

Solutions in the least polar solvents, with the lowest solvating power, have the least effect on spectra (i.e. give spectra most nearly resembling gas spectra) and are least effective in inhibiting vibrational structure. As a consequence, nonpolar liquids such as hydrocarbons are preferred as solvents for spectroscopic studies. The most pronounced solvent effects have been observed for $\pi \rightarrow \pi^*$ transitions in polar molecules. In general the excited state receives predominant contributions from highly polar structures, such as $R_2C^+-O^-$ in ketones, and is consequently more polar than the ground state. Such structures with separated charges are stabilized by solvent polarity according to the electrostatic theory. A polar solvent, therefore, facilitates excitation, and results in a bathochromic shift, as compared with the nonpolar solvent. Only when the ground state is more polar than the solvated excited state (as for example in $n \rightarrow \pi^*$ transitions) a hypsochromic shift would be observed with increasing polar nature of the solvent.

The spectra of nonpolar molecules, such as hydrocarbons, are relatively unaffected by solvent polarity; isooctane and ethanol give

the same values within the limits of error.[2, p. 199] The fact that a bathochromic shift was observed for all the allylsilane compounds when the solvent was changed from isooctane to ethanol would possibly indicate the presence of a polar interaction, such as, for example, XI, although this interpretation remains tentative, because the largest solvent shift was observed for A1, showing a definite silicon involvement (see below).

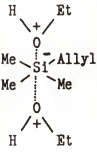


XI

The hypochromic effect observed for the allylsilanes with the change to the more polar solvent is not easily explained. There is currently no satisfactory theoretical approach to the problem of spectral intensities in solution.[25] Furthermore, the effects of solvent polarity on extinction coefficients are often contradictory. For example, a change in solvent from ether to methanol for benzophenone derivatives ($\pi \rightarrow \pi^*$ transition) causes both a bathochromic shift and a hyperchromic effect.[26] For the unsaturated aldehyde citral, on the other hand, a change in solvent from hexane to ethanol causes both a bathochromic shift and a hypochromic effect ($\pi \rightarrow \pi^*$ transition).[27] In some cases, intensity changes have been explained: pyridine shows a small bathochromic shift but a considerable hyperchromic effect for the $\pi \rightarrow \pi^*$ transition when the solvent is changed from hexane to ethanol; this effect has been ascribed to hydrogen bonding of solvent molecules to the lone pair of electrons on the nitrogen, because spectra of pyridine in acid solution, where the proton is directly bonded to the nitrogen atom

through the lone pair showed an even higher hyperchromic effect, with practically no change in wavelength.[2, p. 363]

It is possible that ethanol solvates the allylsilanes through expansion of the valence shell of silicon, so that part of the available electrons on the oxygen can be accommodated in the empty d orbitals of silicon (XII). This type of solvation is the electrostatic opposite



XII

of a solvation through hydrogen bonding, known to cause hyperchromic effects. Furthermore, this solvation effect could be expected to be more pronounced for the first term in the series, allyltrimethylsilane, where the smaller methyl groups offer less steric hindrance to coordination with solvent molecules.

Discussion of the Possible Causes of the Shifts Observed

From a study of the structure of the molecules involved and an extensive literature search, it would appear that most likely causes of the shifts observed could be:

1. Structure modification due to replacement of methyl with allyl groups (two more carbons introduced each time).

2. Participation of the silicon d orbitals, leading to interaction with the allylic double bonds.

3. Interspatial homoconjugative interaction of the type proposed[7] for a cyclopolymerization mechanism.

Analysis of Structure Effects

Every time that a methyl group is replaced with an allyl group in the compounds studied the original structure is modified, because two more carbon atoms are introduced in each substitution.

The fairly small value of the shifts obtained could support the objection that they could have been caused by the progressive structure modification occurring. It seemed, therefore, worthwhile to study these structure effects, namely the effect on ultraviolet spectra of the progressive introduction of alkyl groups.

The very little theoretical work carried out on these effects, has been mainly confined to hyperconjugative effects, such as the ones occurring in methyl-substituted ethylenes (Mulliken,[28] 1942). In the allylsilane case, model compounds are limited (i) to compounds containing only one chromophore (to eliminate the possibility of chromophoric interaction) and (ii) to normal alkyl substituents (to maintain a close similarity with the allyl systems studied).

If a compound is substituted with progressively longer alkyl groups, the first substitution (methyl) is expected to bring into play mainly hyperconjugative effects, while the further ones (ethyl, propyl . . .) will bear their influence mainly by inductive effects. The inductive effects appear to increase progressively with increase in length of the alkyl chain, as shown by the increase in dipole moment in the series:[29]

R	RCl Dipole Moment (D)
Me	1.87
Et	2.05
n-Pr	2.10
n-Bu	2.11
n-Pentyl	2.12
n-Heptyl	2.15

and by the decrease in ionization potential (a physical constant closely related to the ultraviolet absorption) in the two series:[30]

Methane	13.1	Ethylene	10.50
Ethane	11.6	Propylene	9.70
Propane	11.3	1-Butene	9.65
Butane	10.34		

However, an examination of available ultraviolet data does not show any definite trends. The gas phase ultraviolet absorption of unsaturated hydrocarbons has been investigated independently by Jones and Taylor[31] and Carr and Pickett.[32-34] The following data were obtained:

	Jones and Taylor		Carr and Pickett	
	λ_{max} (mμ)	E	λ_{max} (mμ)	E
Propene	172.5	11,000	-	-
1-Butene	174.5	11,200	175.2	15,500
1-Pentene	178.0	13,700	176.7	15,350
1-Hexene	177.2	10,800	177.9	10,720

It is clear that, although a bathochromic shift was obtained by both investigations for the first terms, no regular trend is apparent either in wavelength or in extinction coefficients.

Rice[35] studied solvent effects in alkyl-substituted acetones; the following data were reported:

	Neat liquid	Aqueous Solution		Ethanol Solution	
	λ_{max} (mμ)	λ_{max} (mμ)	E	λ_{max} (mμ)	E
Methylacetone	277.0	266.5	20.9	275.0	19.8
Ethylacetone	279.0	269.5	21.2	277.0	21.2
n-Propylacetone	279.0	270.0	21.2	277.0	21.2

In this case, the effects of progressive substitution were nearly negligible. The same conclusion could be arrived at, at least for wavelength, observing the effects of alkyl substitution on the benzene $0 \rightarrow 0$ band, reported by Matsen et al.[36] (solution spectra):

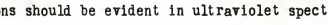
	λ_{max} (mμ)	E
Toluene	268.62	220
Ethylbenzene	268.00	180
n-Propylbenzene	268.15	177
n-Butylbenzene	268.80	170

In conclusion, the allylsilane series studied exhibits definite and regular trends in both wavelength and extinction coefficients, trends missing from the structure effects considered above, but present in series based on conjugative interaction, such as conjugated polyenes and polyene aldehydes.[2, p. 236] However, the synthesis and investigation of n-propylallylsilanes (Chapter IV), where no structure change would occur on progressive allyl substitution, can provide a more definite answer.

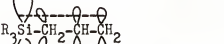
Silicon d Orbitals Participation

Elements on the right in the second row of the periodic system, namely silicon, phosphorus, and sulfur, have available d orbitals with quantum number equal to the valence shell s and p orbitals, which are not occupied in the free atom and are energetically not too far above the valence shell.

These d orbitals can become involved in bonds by expansion of the valence shell, either through formation of double bonds between the central atom (silicon, phosphorus, or sulfur) and another group (e.g. an unsaturated group(or by conjugation of two chromophoric groups through the central atom.[2, p. 467] In either case, the presence of these interactions should be evident in ultraviolet spectra. The first type of interaction would apply to the allylsilanes studied, and could be shown either by charged structures:[37]

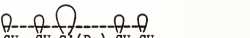


or by $d\pi$-$p\pi$ electron delocalization, because the very diffuse silicon 3d orbitals could extend far enough to overlap the β,γ-conjugated system:[2, p. 475]



The second type of interaction (conjugation through the silicon atom) is less likely to apply to allysilane systems, but could apply to vinylsilanes:

or



It appears of interest to compare similar systems. The most informative systems are the ones containing silicon, "pentavalent" phosphorus or the sulfone group; sulfides are also interesting, but the lone pair of electrons present makes the results more difficult to interpret.

Among the first authors to observe evidence of valence shell expansion, Kohler and Potter[38] found that α,β-unsaturated sulfones showed marked resemblance in chemical behavior with the analogous α,β-unsaturated carbonyl compounds; the sulfonyl group could not participate in the kind of conjugation that is characteristic of α,β-unsaturated ketones without expanding the valence shell of sulfur. Later, Koch[39] and Fehnel and Carmack[40] found that α,β-unsaturated sulfones absorbed at considerable longer wavelengths that was expected from either an isolated SO_2 group or a vinyl group, and ascribed the bathochromic shift to resonance interaction between the two.

When the unsaturated system was insulated by one methylene group, no interaction was observed in the sulfone series, although relatively few compounds have been investigated.[2, p. 481] Benzyl ethyl sulfone, dibenzyl sulfone, and benzylphenyl sulfone were found to absorb at the same wavelength, 265 mμ (main benzene band).[40] Some interaction has been found for β,γ-unsaturated sulfides (allyl and benzyl sulfides); however, even sulfides did not show any interaction when the unsaturated group was two atoms removed from the sulfur.[37, 41]

The spectra of phenylphosphorus derivatives in which the central atom has no lone pair of electrons available (e.g. triphenylphosphine oxide) show a slight conjugative interaction involving expansion of the valence shell, causing a small bathochromic and

hyperchromic shift in the phenyl absorption. However, straight additivity of extinction coefficients and no change in λ_{max} was observed increasing the number of phenyl groups bound to the phosphorus: this indicates a lack of interaction between them. In the series phenylphosphinic acid, diphenylphosphinic acid, and triphenylphosphine oxide, λ_{max} remained constant at 263 mμ, and the extinction coefficients were close to a 1/2/3 ratio.[42]

Some organosilicon substituents have a small bathochromic effect; for example the phenyl absorption of phenyltrimethylsilane in the 240-270 mμ region is shifted 4.5 mμ towards the visible, showing a moderate resonance interaction.[43, p. 485] However, many silicon compounds (triphenylsilane, triphenylsilanol, tetraphenylsilane) absorb at the same wavelength as the corresponding carbon compounds, showing little interaction between silicon and the phenyl ring.[44] It appears that valence shell expansion of silicon requires activating groups: a 7 mμ bathochromic shift (accompanied by a slight hypochromic shift) of the main benzene absorption band was observed in mono-and tri-p-dimethylamino substituted triphenylsilanols; this shift may be ascribed to resonance involving quinoid structures using silicon d orbitals.[44] Trisilylamine, $(H_3Si)_3N$, is a weaker base than trimethylamine although silicon is more electropositive than carbon, because of $\overset{+}{N}=\overset{-}{Si}$ bonding through the d orbitals of silicon.[43, p. 94]

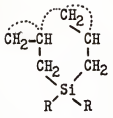
From the limited number of examples available (sulfur and phosphorus series), it would appear that when conjugation involves the d orbitals of a central atom, increasing the number of chromophoric groups bound to the atom does not cause a parallel increase in wavelength

of absorption. For the allylsilane series, on the contrary, progressive λ_{max} shifts were observed with increasing allyl substitution. However, the presence of a silicon - double bond interaction can be verified by an investigation of the ultraviolet spectra of vinylsilanes (Chapter III), where such an interaction should be at its maximum, and of carbon analogues (carbon replacing silicon) of allyl- and vinyl-silanes (Chapter IV), where such an interaction should be clearly absent.

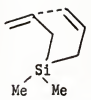
Interspatial Conjugative Interaction

The observation of the ultraviolet absorption of series of conjugated polyenes[2, p. 228-239] shows how the conjugation of two or more chromophores produces a system with new absorption properties, in which both λ_{max} values and extinction coefficients have increased. This increase continues as long as the conjugated system is lengthened, although the rate of increase diminishes as the number of conjugated chromophores becomes larger. The λ_{max} values and the extinction coefficients observed for the allylsilane series seem to resemble this behavior, although the rate of increase of λ_{max} shows a sharper drop.

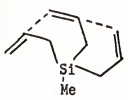
An interspatial conjugative interaction in the allylsilane series could be represented by the general structure XIII, which resolves into XIV, XV, and XVI for A2, A3, and A4 (scale models show how the first and fourth allyl groups on A4 are too far for a full-circle interaction to be possible). The interaction could be defined as a pseudo-butadiene, pseudo-hexatriene, and pseudo-octatetraene type.



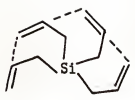
XIII



XIV

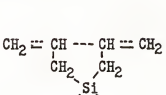


XV



XVI

Alternate five- or seven-membered structures, such as XVII or XVIII, are certainly less stable than six-membered ones, due to poor charge stabilization and some steric strain.[65] For example Bartlett,[66, 77] who studied the solvolyses of 4-pentenyl and 5-hexenyl p-nitrobenzenesulfonates, (i) obtained cyclic products only from the hexenyl derivative, which could form a six-membered ring; (ii) showed how both solvolysis and k/k_{hexyl} rates were much higher for the hexenyl than for the pentenyl derivative. A cyclic intermediate had been postulated for both compounds.



XVII

XVIII

Five- and seven-membered structures are also unlikely to apply to triallyl or tetraallyl systems. The spectroscopic study of allylmethylsilanes showed additional interaction as the number of allyl groups was increased. Extended conjugation in the triallyl system

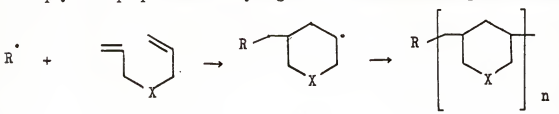
using structures XVII or XVIII requires a bicyclic structure comprising one five- and one seven-membered ring, which appears energetically unfavorable.

Scale models show how extended conjugation for the tetraallyl system, leading to a tricyclic structure, is possible only with six-membered structures, which allow a slightly offset p_σ interaction. The steric requirements of five- and seven-membered structures allow only the formation of two independent bicyclic systems, with a consequent much lower extent of conjugative interaction (the delocalization energy of octatetraene is 1.52 β, which is 38 per cent higher than the delocalization energy of two independent butadiene systems, 0.94 β).

The lower extent of interaction possible with a p_σ model could explain the fairly small value of the shifts obtained; a second reason could be that the freedom of rotation of the allyl chains would reduce the probability of intramolecular interaction. Ireland and Schiess,[47] who studied ultraviolet interactions in $\beta\gamma$-unsaturated ketones, ascribed the small order (1-2 mμ) of the bathochromic shifts obtained to the free rotation about the vinyl group bond possible in their systems; Labhart and Wagniere,[48] who investigated β,γ-unsaturated ketones which were part of cyclic structures, obtained substantial bathochromic shifts.

Polyallyl compounds are known to polymerize by an intra-intermolecular mechanism to give methylene-linked mono, bi, and tricyclic rings (from diallyl, triallyl, and tetraallyl monomers respectively), as shown by Butler and Angelo[11] for various diallyl compounds, Butler and Stackman,[21] and Marvel and Woolford[22] for diallyldimethylsilane, Trifan and Hoglen[23] for tri- and tetraallyl ammonium bromide, triallylmethylsilane, and 3-vinyl-1,5-hexadiene, and by Kropa[24] for tetraallylsilane.

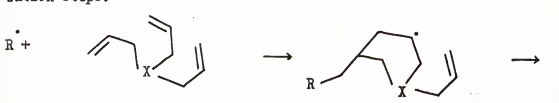
Butler and Angelo[11] proved that XX was the repeating unit in polymers obtained from diallyl systems, XIX being the transition state proposed (for free-radical initiators). Trifan and Hoglen[23] concluded from physical properties and hydrogenation studies of the polymers that



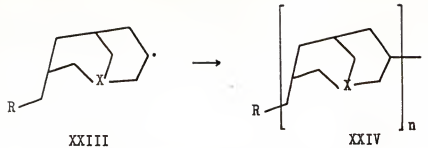
XIX XX

for triallyl derivatives, including triallylmethylsilane, polymerization occurred mainly through sequence XXI-XXIV, XXII and XXIII being the transition states, and that with tetraallyl derivatives radical XXIII propagated once again intramolecularly to form a bridged tricyclic repeating unit.

It is seen that the structures drawn for the cyclopolymerization transition states coincide with the structures depicting the interspatial conjugative interaction proposed for the allylsilanes under ultraviolet excitation. The free-radical notation is meant to be only indicative, because, as shown for example by Field,[67] cyclopolymerization can occur by free-radical, anionic, or cationic mechanisms. The existence of this interspatial conjugative interaction in the excited state of polyallyl systems could explain the very high intramolecular vs. intermolecular selectivity shown by these monomers in the repetitive cyclization steps.



XXI XXII



XXIII XXIV

A possible confirmation of the identity of the transition state of cyclopolymerization with the ultraviolet conjugative interaction proposed for the allylsilanes comes from kinetic studies by Mikulasova and Hrivik[68-69] of the free-radical polymerization of A1, A2, A3, and A4. The authors found that the activation energy per double bond for the polymerization of the allylsilanes had the values reported in Table 9. It is seen that the ΔE_a ratios approach the shift ratios obtained from the ultraviolet spectroscopic study of the compounds.

TABLE 9

ACTIVATION ENERGIES[b] PER DOUBLE BOND FOR THE POLYMERIZATION OF ALLYLMETHYLSILANES ACCORDING TO MIKULASOVA AND HRIVIK[68-69]

Compound	E_a	E_a Average	ΔE_a	ΔE_a Ratio (ΔE_a A1-A2 set at 1)
A1	34-35	34.50		
			9.65	1.00
A2	24.5-25.2	24.85		
			4.35	0.45
A3	20-21	20.50		
			1.35	0.14
A4	18.8-19.5	19.15		

[b] kcal./mole

Calculation of Shift Ratios by Molecular Orbital Theory

The frequency of ultraviolet absorption of conjugated polyene and polyene aldehydes has been correlated with the HMO (Huckel Molecular Orbital Theory) energy difference between the highest occupied and lowest unoccupied energy levels, corresponding to the most important $\pi \rightarrow \pi^*$ transition.[46, p. 207]

This HMO energy difference (Δm) - frequency correlation is linear, and therefore the shift ratios of the Δm values calculated for a polyene series should be the same as the shift ratios of the ultraviolet absorption frequencies obtained for the polyenes. The Δm values, however, cannot give directly the frequency of absorption of an unknown series, because the slope of the correlation line has to be obtained by plotting frequencies obtained empirically vs. calculated Δm values.

An application of this correlation to the allylsilane series assumes that the amount of perturbation introduced by the presence of the central silicon atom applies equally to all four allylsilanes; all the factors influencing the partial bonds of structures XIV-XVI (bond distances, bond angles, extent of p_π or p_σ interaction) would influence the four allylsilanes in equal amount, so that these factors cancel out in the ratios.

As a check, the Δm values for the pseudo-butadiene, pseudo-hexatriene, and pseudo-octatetraene structures postulated have been calculated (see Appendix) using a k value of 0.6 β for the partial bond. This value is meant to be only indicative, and was chosen after consideration of the slightly offset p_σ interactions which appear feasible in

scale models of the allylsilanes, of the k value of 0.3 β proposed by Woods, Carboni and Roberts[45] for the part π and part σ contributions in 7-norbornenyl cations, and of the k value of 0.7-0.8 β proposed for the p_σ interactions of the extended π systems in Fukui's copolymerization models.[46, p, 410]

The results obtained are reported in Table 10, together with the Δm shifts ($\Delta\Delta m$) and the Δm shift ratios (ethylene corresponds to the mono-allyl compound; the Δm values for k (partial bond) = β are from Streitwieser.[46, p. 208)]

TABLE 10

HMO CALCULATIONS

Structure	k(partial bond)= β[a]			k(partial bond)=0.6β[b]		
	Δm	$\Delta\Delta m$	$\frac{\Delta\Delta m}{\text{Ratio}}$	Δm	$\Delta\Delta m$	$\frac{\Delta\Delta m}{\text{Ratio}}$
Ethylene	2.000	0.764	1.000	2.00	0.51	1.000
Pseudo-butadiene	1.236	0.346	0.453	1.48	0.23	0.451
Pseudo-hexatriene	0.890	0.195	0.256	1.26	0.13	0.255
Pseudo-octatetraene	0.695			1.13		

[a]From Streitwieser.[46, p. 208]

[b]The calculations from which these values have derived are reported in Appendix.

If the correlation and the interaction model hold, the data shown in Table 10 would predict a 1.00/0.45/0.25 shift ratio for the absorption frequencies of the allylsilane series. Furthermore, a linear correlation between frequencies and Δm values would suggest the presence of a conjugative interaction.

TABLE 11

FREQUENCY VALUES OF ALLYLMETHYLSILANES[a]

Compound	Isooctane				Ethanol				Gas Phase			
	λ	ν	ν Shift	ν Shift Ratio	λ	ν	ν Shift	ν Shift Ratio	λ	ν	ν Shift	ν Shift Ratio
A1	192.3	52002			193.6	51652			188.7	52994		
			641	1.000			502	1.000			280	1.000
A2	194.7	51361			195.5	51150			189.7	52714		
			263	0.410			260	0.518			111	0.396
A3	195.7	51098			196.5	50890			190.1	52603		
			130	0.203			129	0.257			-	-
A4	196.2	50968			197.0	50761			-	-		

[a] λ in mμ, ν in $cm.^{-1}$

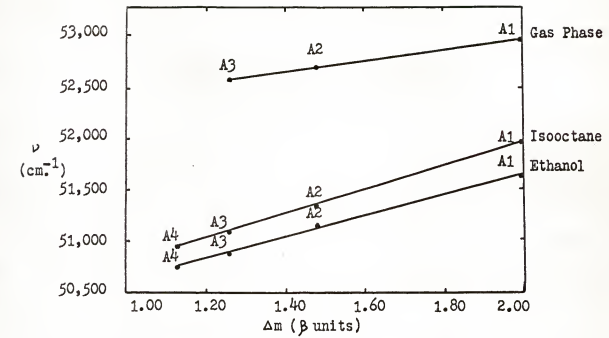


Figure 4.— Δm - frequency correlation. Allylmethylsilanes.

The frequency values for the allylsilane series have been reported in Table 11. It is seen that the frequency shift ratios approach the ΔΔm ratios. The frequencies have been plotted vs. Δm values ($k_{___}$ = 0.6) in Figure 4: straight line correlations were obtained.

CHAPTER III

RESULTS AND DISCUSSION OF THE VINYLMETHYLSILANES STUDY

Choice of Solvents

The vinylsilane compounds studied absorbed in the 175-180 mμ region. This region approaches the useful limit of solution spectra (172 mμ[50]). After their absorbance in the far ultraviolet was determined (Table 12), two solvents, n-heptane and acetonitrile, were found suitable. Solution spectra were run in the thinnest cells available (0.03 mm.) to minimize solvent absorption.

TABLE 12

ABSORBANCE[a] OF n-HEPTANE AND ACETONITRILE IN THE FAR ULTRAVIOLET

Wavelength (mμ)	n-Heptane	Acetonitrile
200	0.00	0.00
195	0.01	0.00
190	0.02	0.00
185	0.03	0.01
180	0.03	0.11
177.5	0.04	0.22
175.7[b]	0.04	0.31

[a] Solvent vs. nitrogen; path length 0.03 mm.

[b] λ_{max} for acetonitrile.

Heptane Solutions

The ultraviolet absorption of heptane solutions of trimethylvinylsilane (V1), dimethyldivinylsilane (V2), methyltrivinylsilane (V3), and tetravinylsilane (V4) (all known compounds) was determined. The values obtained are shown in Tables 13 and 14. All the compounds absorbed in the 175-180 mμ region, giving absorption bands less broad than the allylsilane ones, with extinction coefficients ranging from 15,000 to 40,000. Absorbance was plotted *vs.* molarity for four concentrations to check the adherence to Beer's law (Figure 5): good adherence was obtained.

TABLE 13

λ_{max} AVERAGES OF VINYLMETHYLSILANES (HEPTANE SOLUTIONS)

Compound	λ_{max} Average (mμ)	Departures from Average	Shift Average (mμ)
V3	176.8	± 0.3%	0.1
V4	176.9	± 0.6%	0.8
V2	177.7	± 0.1%	0.8
V1	178.5	± 0.1%	

Observation of Table 13 shows that, although the compounds did not absorb at the same wavelength, the shifts obtained were very small (maximum total shift, V1-V3, 1.7 mμ), and did not seem to follow any particular trend with respect to increasing vinyl substitution (V3 absorbed at the shortest wavelength, V1 at the longest).

TABLE 14

EXTINCTION COEFFICIENT AVERAGES OF VINYLMETHYLSILANES
(HEPTANE SOLUTIONS)

Compound	E Average	Departures from Average	Additivity (E_{A1} set at 1)
V1	18,905	± 1%	1.0
V2	28,395	± 1%	1.5
V3	34,252	± 1%	1.8
V4	38,553	± 1%	2.0

The extinction coefficients observed (Table 14) increased with increasing vinyl substitution, but the increase was progressively smaller, and always remained far short of straight additivity. The ratios obtained, 1.0/1.5/1.8/2.0, correspond to a rate of increase of 50, 20, and 11 per cent respectively.

Acetonitrile Solutions

The spectroscopic data obtained for the acetonitrile solutions of the vinylsilanes have been reported in Tables 15 and 16. Absorbance was plotted *vs.* molarity for four concentrations to check the adherence to Beer's law (Figure 6): good adherence was obtained.

Table 15 shows how all the λ_{max} values were shifted bathochromically with respect to the values obtained for the heptane solutions. The shifts obtained were also smaller (maximum total shift, V1-V4, 0.7 mμ), and not only did not seem to follow any particular trend with respect to increasing vinyl substitution, but were not in the same order observed for the heptane solutions (V3 absorbed at a longer wavelength in acetonitrile).

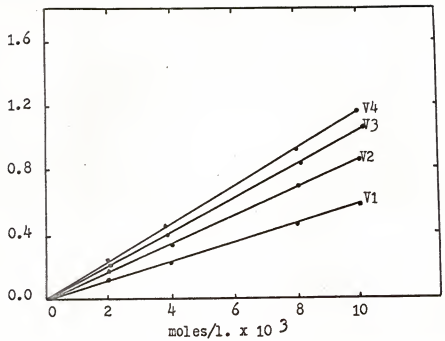


Figure 5.—Adherence to Beer's law of vinylmethylsilanes (heptane solutions).

TABLE 15

λ_{max} AVERAGES OF VINYLMETHYLSILANES (ACETONITRILE SOLUTIONS)

Compound	λ_{max} Average (mμ)	Departures from Average	Shift Average (mμ)
V4	178.6	± 0.2%	0.1
V2	178.7	± 0.2%	0.1
V3	178.8	± 0.2%	0.5
V1	179.3	± 0.2%	

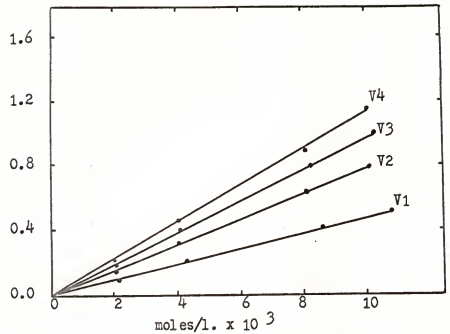


Figure 6.—Adherence to Beer's law of vinylmethylsilanes (acetonitrile solutions).

TABLE 16

EXTINCTION COEFFICIENT AVERAGES OF VINYLMETHYLSILANES (ACETONITRILE SOLUTIONS)

Compound	E Average	Departures from Average	Additivity (E_{V_1} set at 1)
V1	15,409	± 5%	1.0
V2	25,553	± 3%	1.6
V3	31,862	± 4%	2.1
V4	36,520	± 5%	2.4

All the extinction coefficients obtained for the acetonitrile solutions (Table 16) showed hypochromic effects over the corresponding heptane solutions. The effect was more pronounced for the first terms, so that the ratios became 1.0/1.6/2.1/2.4, with a rate of increase slightly higher than for the heptane solutions.

Gas Phase

A complete spectroscopic study in the gas phase of the first three compounds in the vinylsilane series was possible; the low vapor pressure of the fourth compound, tetravinylsilane, allowed only a qualitative study (determination of λ_{max} but not of the extinction coefficient).

The spectroscopic data are reported in Tables 17 and 18. Similarly to the solution spectra, absorption bands were obtained. The V1 absorption band was resolved in the gas phase into a main peak and a shoulder, 1.9 mμ apart, with close intensities. Absorbance was plotted *vs.* molarity for four concentrations to check the adherence to Beer's law (Figure 7): fairly good adherence was obtained; the slight scattering of some of the points is most likely due to the difficulty in measuring exact pressures.

TABLE 17

λ_{max} VALUES OF VINYLMETHYLSILANES (GAS PHASE)

Compound	λ_{max} (mμ)	Shift (mμ)
V4	175.2	0.4
V1 shoulder	175.6	0.2
V2	175.8	0.1
V3	175.9	1.6
V1	177.5	

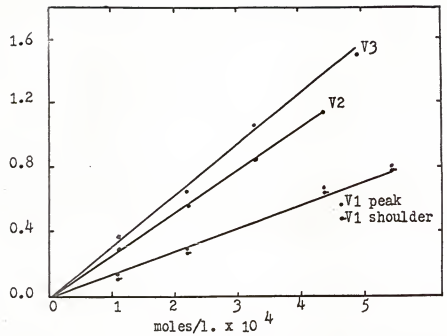


Figure 7.—Adherence to Beer's law of vinylmethylsilanes (gas phase).

TABLE 18

EXTINCTION COEFFICIENT AVERAGES OF VINYLMETHYLSILANES (GAS PHASE)

Compound	E Average	Departures from Average	Additivity (E_{V1} set at 1)
V1 peak	13,717	± 9%	1.0
V2	26,047	± 2%	1.9
V3	31,577	± 7%	2.3
V1 shoulder	13,157	± 12%	-

Due to the different technique involved in the determination of gas phase spectra (see experimental part), the λ_{max} values reported are those of the sharpest bands (highest pressures). All the vinylsilanes absorbed at lower wavelength in the gas phase than in solution; V1

appeared to be shifted bathochromically from the rest of the vinylsilanes, which showed very close absorptions. The total maximum shift, V1-V4, was 2.3 mμ, higher than any observed for solution spectra.

The extinction coefficients (first three terms) were generally smaller than the ones obtained from solution spectra. The ratios, 1.0/1.9/2.3, showed that V2 was only 10 per cent short of straight additivity, while V3 was 23 per cent short.

Comparison with the Results of the Allylmethylsilanes Study

A comparison of the spectroscopic data obtained with the allylmethylsilanes and the ones obtained with the vinylmethylsilanes shows that for the vinylmethylsilanes:

(i) No regular trend was observed with increasing vinyl substitution.
(ii) The shifts obtained were smaller.
(iii) The first compound in the vinylsilane series, V1, absorbed at the longest wavelength, while the first compound in the allylsilane series, A1, absorbed at the shortest wavelength.
(iv) The only significant shift obtained was between V1 and the rest of the vinylsilanes grouped together.
(v) The shifts obtained in the gas phase were larger than the ones obtained in solution, while the reverse was true for the allysilanes.
(vi) The extinction coefficients were higher in absolute value than the ones observed for the allysilanes, but were much shorter of straight additivity.

Discussion

Scale models of the four vinylsilanes show that no interspatial conjugative interaction of the type proposed for allysilanes is possible. On the other hand, if silicon - double bond interactions through use of the silicon d orbitals (valence shell expansion) occur, they should be clearly shown in the vinyl series, due to the immediate contact of the interacting systems.

The interaction of the silicon atom with the C=C double bond ($p\pi - d\pi$ interaction, Figure 8) is, however, expected to be small, and can be compared with a similar interaction of the sulfone group in ethylvinyl sulfone and divinyl sulfone.[51, p. 96] For both silicon atom and sulfone group the interaction observed is only a small fraction of a C=C-C=C or C=C-C=O type of conjugation. The silicon and sulfone type of interaction involve a three atom conjugated system:

$$CH_2=CH-\dot{S}i- \longrightarrow CH_2^{-}-CH=\dot{S}i-$$

while a butadiene type involves four atoms:

$$-\dot{C}=\dot{C}-\dot{C}=\dot{C}- \longrightarrow -\dot{C}=\dot{C}-\dot{C}=\dot{C}-$$

Conjugation through the silicon atom (see Chapter II), which would extend the conjugated system, does not seem to be operating in the similar systems reviewed in Chapter II. It has been mentioned above how phenylphosphorus derivatives where phosphorus has no lone pair of electrons available show a bathochromic shift of the benzene band, but no additional shifts as the phenyl groups bound to the phosphorus increase from one to three.[42] Koch[39] found the phenyl groups in diphenyl sulfone perpendicular to each other, thereby excluding any conjugative interaction between them.

It also appears from the results of the phenylphosphorus series that, although three d orbitals are useful for a $p\pi - d\pi$ interaction with adjacent atoms,[51, p. 3] a substantial interaction occurs with only one group, subsequent interaction with the remaining groups being negligible.

A similar behavior seems evident in the vinylsilane series, where one actually goes a step further, because the amount of silicon interaction was actually higher for the first term than for the others. This

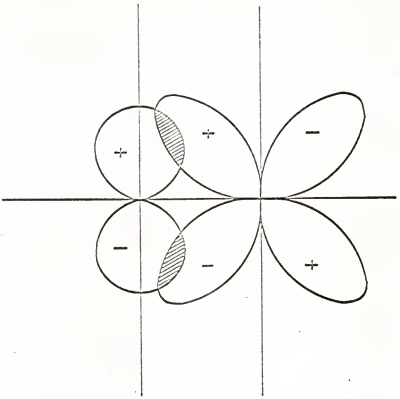


Figure 8.—$p\pi - d\pi$ Interaction

was shown by the fact that the only significant shift obtained (1.6 mμ in the gas phase) was between V1 and the rest of the vinylsilanes, which were grouped together, and that the shift was bathochromic, an indication of a lower energy excited state available to the compound. Particularly significant is the fact that the V1 absorption in the gas phase showed a peak and a shoulder, a behavior not shared by the other vinylsilanes, and typically indicative of the presence of an interaction. The only indication of some participation of more than one vinyl group in the silicon interaction is the fact that the extinction coefficients were progressively shorter of straight additivity; this shows how the probability of ultraviolet transitions is progressively decreasing from V1 to V4, a possible indication of some interaction participation in the lower terms.

The comparison with the results obtained from the allylmethylsilane series showed a widely different behavior. Very small shifts were obtained for the vinylsilane series, where the silicon - double bond interaction should be at its maximum; if such an interaction could extend far enough to involve an allyl group, its influence would be even smaller, and could be expected to be of some importance only for the first term in the series, allyltrimethylsilane. The only spectroscopic evidence obtained in support of the last statement could be the bathochromic shift observed for A1 with a change in solvent from isooctane to ethanol. This shift was 0.5 mμ larger than for the other allylsilanes; polar solvent stabilization of charged structures present in a silicon - allyl interaction could have contributed to it.

CHAPTER IV

RESULTS AND DISCUSSION OF THE CARBON ANALOGUES STUDY

Synthesis of 4,4-Dimethyl-1,6-heptadiene

Out of the four carbon analogues studied, three, 3,3-dimethyl-1-butene (V1C), 3,3-dimethyl-1,4-pentadiene (V2C), and 4,4-dimethyl-1-pentene (A1C) were known compounds. The fourth, 4,4-dimethyl-1,6-heptadiene (A2C), had not been previously made.

The synthetic routes which were tried for the synthesis of A2C have been reported in the following pages. They can be divided into five main groups:

(i-v) Halogen substitution reactions. Only unidentified mixtures of products were obtained.

(vi) Malonic ester substitution, following Marvel's preparation of 1,6-heptadiene.[52] The S_N2 reaction was inhibited by steric hindrance.

(vii-x) Substitution reactions on the tosylate of 2,2-dimethyl-4-penten-1-ol.[53] Only unidentified mixtures of products and/or reformed 2,2-dimethyl-4-penten-1-ol were obtained.

(xi-xvii) Reduction of the ditosylate of 4,4-bis-(hydroxymethyl)-1,6-heptadiene. Reductions carried out at high temperatures gave the desired product, 4,4-dimethyl-1,6-heptadiene (A2C), plus smaller yields of 4-methyl-4-hydroxymethyl-1,6-heptadiene; however, the product obtained was slightly impure, and the high temperature led to difficult control and reproducibility of the reaction.

(xviii) Wolff-Kishner reduction of 2-allyl-2-methyl-4-pentenal. This reaction afforded gas-chromatographically pure A2C. The aldehyde (a new product) was prepared following the procedure outlined by Saunders[54] and Brannock[53] for similar compounds. The identity of A2C was proved by elementary, infrared, and nuclear magnetic resonance analyses.

The new products synthesized have been listed in Table 19.

(i) $BrCH_2-C(CH_3)_2-CH_2-Br + CH_2=CH-MgBr \longrightarrow$ u.m.p.

(ii) $BrCH_2-C(CH_3)_2-CH_2-Br + CH_2=CH-Li$[57] (ether soln.) $\longrightarrow$ u.m.p.

(iii) $BrCH_2-C(CH_3)_2-CH_2Br + CH_2=CH-Li$ (solid) $\longrightarrow$ u.m.p.

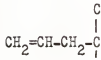
(iv) $Cl-C(CH_3)_2-Cl + CH_2=CH-CH_2-Li$[58] $\longrightarrow$ u.m.p.

(v) $(CH_3)_2C=O + CH_2=CH-CH_2-MgBr \longrightarrow CH_2=CH-CH_2-C(CH_3)_2-OH$ a

74%

(vi) $CH_2(COOC_2H_5)_2 + BrCH_2-C(CH_3)_2-CH_2-Br \xrightarrow{NaOEt} CH_2(COOC_2H_5)-CH_2-C(CH_3)_2-CH_2-CH(COOC_2H_5)_2$ b

65%

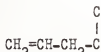


n.p., 90%

(vii)

(viii)

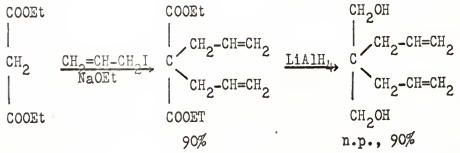
(ix)

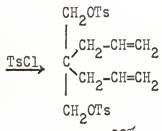


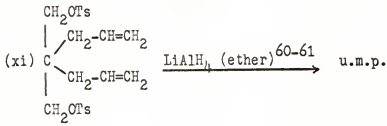
32%

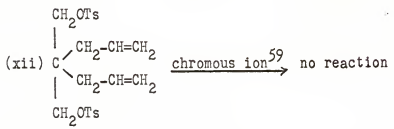
(x)

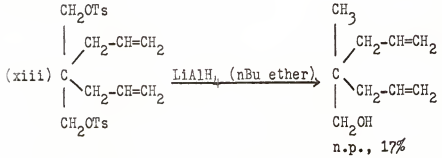
20%

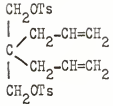

COOEt
CH2
COOEt
CH2=CH-CH2I
NaOEt
COOEt
CH2-CH=CH2
CH2-CH=CH2
COOET
90%
LiAlH4
CH2OH
CH2-CH=CH2
CH2-CH=CH2
CH2OH
n.p., 90%


TsCl
CH2OTs
CH2-CH=CH2
CH2-CH=CH2
CH2OTs
n.p., 90%

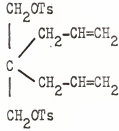

(xi)
CH2OTs
CH2-CH=CH2
CH2-CH=CH2
CH2OTs
LiAlH4 (ether) 60-61
u.m.p.


(xii)
CH2OTs
CH2-CH=CH2
CH2-CH=CH2
CH2OTs
chromous ion 59
no reaction

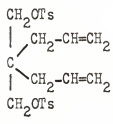

(xiii)
CH2OTs
CH2-CH=CH2
CH2-CH=CH2
CH2OTs
LiAlH4 (nBu ether)2
CH3
CH2-CH=CH2
CH2-CH=CH2
CH2OH
n.p., 17%

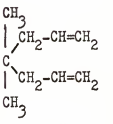
(xiv) 

$\xrightarrow{LiH/LiAlH_4\ (THF)}$[62] u.m.p.

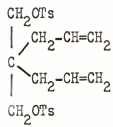
(xv) 

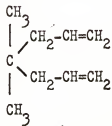
$\xrightarrow{LiH/LiBH_4\ (THF)}$[63] no reaction

(xvi) 

$\xrightarrow{LiH/LiBH_4\ (DMEE,\ 145^{\circ})}$ 

n.p., 3%

(xvii) 

$\xrightarrow{LiAlH_4\ (DMEE,\ 145^{\circ})}$ 

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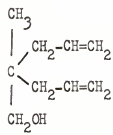
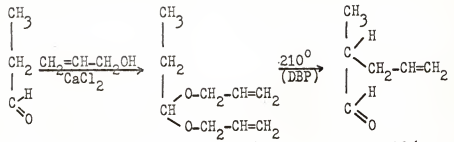
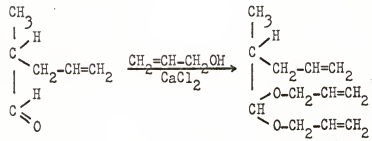
29%



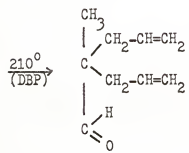
16%



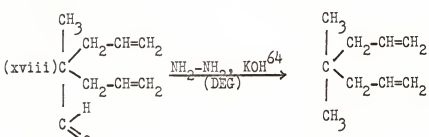
n.p., 68% n.p., 48%



n.p., 63%



n.p., 66%



76%

Notes:

[a] For conversion to the bromide, to be reacted with allyl Grignard. The work was discontinued in view of the poor results obtained by Russian workers[55, 56] with similar experiments.

[b] Trace, not identified.

u.m.p.	Unidentified mixture of products	n.p.	New product
THF	Tetrahydrofuran	DMEE	1,2-bis-(2-methoxyethoxy)-ethane
DBP	Dibutyl phthalate	DEG	Diethylene glycol

TABLE 19

NEW PRODUCTS SYNTHESIZED

Compound	b.p.		n_D^{20}	d_4^{20}	Analytical[a]				% Yd.
					Calculated		Found		
	°C	Press. (mm.)			C	H	C	H	
4,4-Bis-(hydroxymethyl)-1,6-heptadiene	89	0.3	1.4859	0.9933	69.19	10.32	69.74	10.15	90
4,4-Bis-(hydroxymethyl)-1,6-heptadiene ditosylate[b]	71.5-72.5[c]	-	-	-	59.46	6.07	59.63	6.10	90
2,2-Dimethyl-4-penten-1-tosylate[d]	e	-	1.5071	1.0867	62.65	7.51	62.80	7.46	90
4-Methyl-4-hydroxymethyl-1,6-heptadiene	41-42	0.6	1.4644	0.8717	77.09	11.50	77.42	11.49	17
Propionaldehyde diallyl acetal	85	45	1.4277	0.8713	69.19	10.32	69.27	10.32	68
2-Methyl-4-pentenal[f]	45	51	1.4204	0.8397	73.42	10.27	73.10	10.38	48
2-Methyl-4-pentenal diallyl acetal	99	19	1.4456	0.8797	73.43	10.27	74.28	10.37	63
2-Allyl-2-methyl-4-pentenal[g]	58	12	1.4482	0.8597	78.21	10.21	78.60	10.24	66
4,4-Dimethyl-1,6-heptadiene	63	90	1.4283	0.7427	87.01	12.98	87.19	12.83	76

[a]The analytical results were confirmed by the infrared spectra of the compounds.

[b]S, calculated: 13.82; found: 13.88.

[c]Melting point.

[d]S, calculated: 11.95; found: 12.06.

[e]Decomposes.

[f]2,4-Dinitrophenylhydrazone, m.p. 101-102°.

[g]2,4-Dinitrophenylhydrazone, m.p. 115-116°.

Solution Spectra of Carbon Analogues of Allylmethylsilanes

The ultraviolet absorption of heptane and acetonitrile solutions of 4,4-dimethyl-1-pentene (A1C) and 4,4-dimethyl-1,6-heptadiene (A2C) was determined. The values obtained are shown in Tables 20 and 21. The compounds absorbed in the 180-185 mμ region, with extinction coefficients ranging from 9,000 to 22,000. Absorbance was plotted *vs.* molarity for four concentrations to check the adherence to Beer's law (Figure 9): good adherence was obtained.

TABLE 20

λ_{max} AVERAGES OF CARBON ANALOGUES OF ALLYMETHYLSILANES (SOLUTION SPECTRA)

Compound	Solvent	λ_{max} Average (mμ)	Departures from Average	Shift Average (mμ)
A1C	heptane	180.4	± 0.1%	1.5
A2C	heptane	181.9	± 0.1%	
A1C	acetonitrile	181.6	± 0.1%	1.1
A2C	acetonitrile	182.7	± 0.1%	

Table 20 shows that a bathochromic shift was observed between the monoallyl and the diallyl compound. The change in solvent from heptane to acetonitrile caused a bathochromic wavelength shift which was more pronounced for A1C (1.2 mμ) than for A2C (0.8 mμ); as a consequence, the A2C-A1C shift was smaller.

Table 21 shows that for heptane solutions the extinction coefficient for A2C remained below straight additivity. The change in solvent from heptane to acetonitrile caused hypochromic effects which

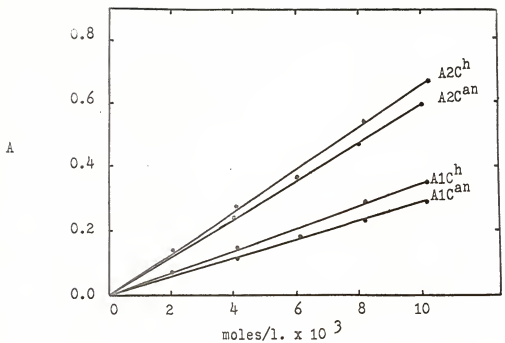


Figure 9.—Adherence to Beer's law of carbon analogues of allylmethylsilanes (solution spectra).

^{h}heptane

^{an}acetonitrile

TABLE 21

EXTINCTION COEFFICIENT AVERAGES OF CARBON ANALOGUES OF ALLYLMETHYLSILANES (SOLUTION SPECTRA)

Compound	Solvent	E Average	Departures from Average	Additivity (E_{A1C} set at 1)
A1C	heptane	11,629	± 3%	1.0
A2C	heptane	22,138	± 1%	1.9
A1C	acetonitrile	9,576	± 4%	1.0
A2C	acetonitrile	19,893	± 2%	2.1

were more pronounced for A1C (18 per cent decrease) than for A2C (11 per cent decrease); as a consequence, the A2C/A1C ratio became larger.

Gas Phase Spectra of Carbon Analogues of Allylmethylsilanes

The fairly high vapor pressure of A1C and A2C allowed a complete spectroscopic study in the gas phase. The absorption bands of both A1C and A2C were resolved in the gas phase into shoulders and a main peak. The spectroscopic data are reported in Tables 22 and 23.

TABLE 22

GAS PHASE SPECTROSCOPIC DATA OF CARBON ANALOGUES OF ALLYLMETHYLSILANES (MAIN PEAK)

Compound	λ_{max} (mμ)	λ_{max} Shift (mμ)	E Average	E Departures from Average	E Additivity (E_{A1C} set at 1)
A1C	178.5	1.2	10,492	± 8%	1.0
A2C	179.7		23,720	± 23%	2.3

Absorbance was plotted *vs.* molarity for four concentrations to check the adherence to Beer's law (Figure 10). The deviations observed for the low concentration values are most likely due to the error introduced by an incomplete evacuation of the cells before filling; the importance of this error increases with decreasing concentrations (pressures) of material, as shown by the large departures from average observed for the extinction coefficients of A2C (Table 22). Only low concentrations could be used for this compound due to its lower vapor pressure; the gas phase extinction coefficient of A2C is therefore to be considered only indicative.

TABLE 23

GAS PHASE SPECTROSCOPIC DATA OF CARBON ANALOGUES OF ALLYLMETHYLSILANES (SHOULDERS)

Compound	λ_{max} (mμ)	E
A1C	172.6	9,140
A1C	183.1	7,998
A1C	189.7	2,666
A2C	171.8	15,082
A2C	184.6	17,138
A2C	189.8	7,998

Table 22 shows that both compounds absorbed at lower wavelength in the gas phase than in solution. The A2C-A1C shift observed was smaller than the one observed in heptane solution.

Although the shoulders observed for the two compounds (Table 23) showed some analogy in wavelength position, no definite trend was apparent.

Discussion of the Allylmethylsilane Carbon Analogues Study

The spectroscopic data obtained for the two carbon analogues of allylmethylsilanes, especially the bathochromic shift between the monoallyl and the diallyl compound, and the values of the extinction coefficient in non-polar and polar solvents, show a clear similarity of behavior when compared with the spectroscopic data obtained for the allylmethylsilanes (Chapter II). It would therefore appear that silicon

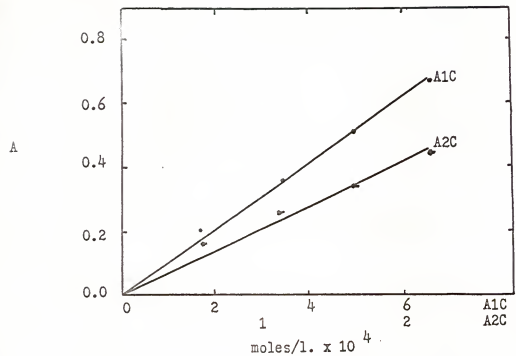


Figure 10.—Adherence to Beer's law of carbon analogues of allylmethylsilanes (gas phase).

interaction is excluded as a possible cause of the bathochromic shifts observed in the allylmethylsilane series.

Silicon interaction is, however, responsible for the fact that the allylsilanes absorbed at a longer wavelength (average shift: 10 mu) than the carbon analogues. As discussed in Chapters II and III, the results of the vinylsilanes study and the comparison with similar systems would indicate that the silicon interaction involves mainly one unsaturated group, subsequent interaction with the remaining groups being negligible. In the vinylsilane case, the amount of silicon interaction remained constant throughout the series. On the basis of these data, it is proposed that the amount of silicon interaction does not vary as the number of allyl groups present increases, and such interaction is, therefore, not responsible for the progressive bathochromic shifts observed in the allylmethylsilane series.

No shoulders were observed in the gas phase spectra of the allylmethylsilanes. The shoulders exhibited by the gas phase spectra of A1C and A2C indicate the presence of submerged bands possibly caused by vibrational interactions making possible forbidden transitions.[2, p. 129] These interactions could be inhibited by the silicon atom, which would insulate from each other the groups attached to the central atom.

The insulating effect could also account for the fact that the diallyl-monoallyl shift was smaller for the carbon analogues than for the allylmethylsilanes. Hyperconjugative interactions on the A2C carbon chain, making possible a linear conjugated system, could reduce the probability of interspatial interactions.

Ultraviolet Absorption of Carbon Analogues of Vinylmethylsilanes

The ultraviolet absorption of heptane and acetonitrile solutions of 3,3-dimethyl-1-butene (V1C) and 3,3-dimethyl-1,4-pentadiene (V2C) was determined. The values obtained are shown in Tables 24 and 25. The compounds absorbed in the 175-180 mμ region, with extinction coefficients ranging from 10,000 to 20,000. Absorbance was plotted *vs.* molarity for four concentrations to check the adherence to Beer's law (Figure 11): good adherence was obtained.

The high vapor pressure of V1C and V2C allowed a complete spectroscopic study in the gas phase.* The absorption bands of V1C and V2C showed the appearance of shoulders; furthermore, the V1C

*The ultraviolet spectrum of V1C in the gas phase had been previously reported by Jones and Taylor.[31] The authors, who used a vacuum ultraviolet spectrophotometer, reported the same absorption maxima, and extinction coefficients slightly lower, than the ones shown in the present work.

TABLE 24

λ_{max} AVERAGES OF CARBON ANALOGUES OF VINYLMETHYLSILANES (SOLUTION SPECTRA)

Compound	Solvent	λ_{max} Average (mμ)	Departures from Average	Shift Average (mμ)
V2C	heptane	175.5	± 0.1%	2.3
V1C	heptane	177.8	± 0.1%	
V2C	acetonitrile	178.4	± 0.1%	0.6
V1C	acetonitrile	179.0	± 0.1%	

TABLE 25

EXTINCTION COEFFICIENT AVERAGES OF CARBON ANALOGUES OF VINYLMETHYLSILANES (SOLUTION SPECTRA)

Compound	Solvent	E Average	Departures from Average	Additivity (E_{V1C} set at 1)
V1C	heptane	15,431	± 2%	1.0
V2C	heptane	19,550	± 3%	1.3
V1C	acetonitrile	10,760	± 3%	1.0
V2C	acetonitrile	15,780	± 2%	1.5

absorption was resolved into two peaks (see Figure 13). The spectroscopic data are reported in Tables 27 and 27. When absorbance was plotted vs. molarity for four concentrations (Figure 12), it was found that the compounds showed fairly good adherence to Beer's law.

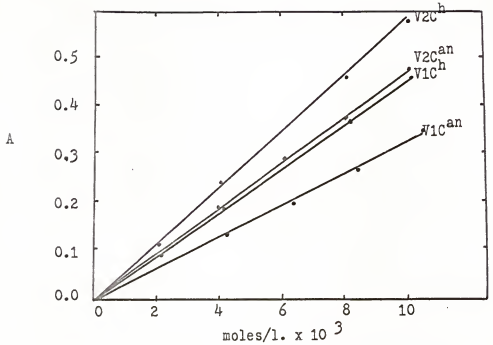


Figure 11.—Adherence to Beer's law of carbon analogues of vinylmethylsilanes (solution spectra).

^{h}heptane

^{an}acetonitrile

TABLE 26

GAS PHASE SPECTROSCOPIC DATA OF CARBON ANALOGUES OF VINYLMETHYLSILANES (MAIN PEAKS)

Compound	λ_{max}	E Average	E Departures from Average
V1C main peak	174.7	12,210	± 10%
V1C second peak	187.7	4,120	± 9%
V2C	176.4	15,699	± 3%

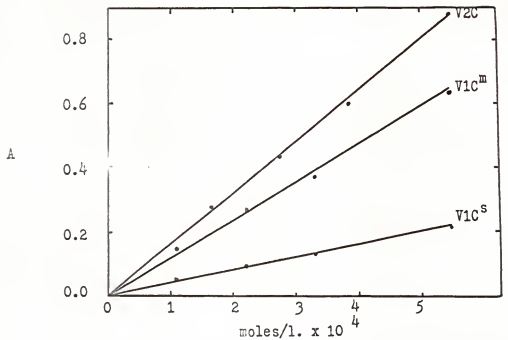


Figure 12.—Adherence to Beer's law of carbon analogues of vinylmethylsilanes (gas phase).

^{m}main peak

^{s}second peak

TABLE 27

GAS PHASE SPECTROSCOPIC DATA OF CARBON ANALOGUES OF VINYLMETHYLSILANES (SHOULDERS)

Compound	λ_{max} (mμ)	E
V1C	171.9	11,279
V1C	183.6	7,038
V1C	188.7	3,748
V2C	173.1	15,356
V2C	186.7	9,780

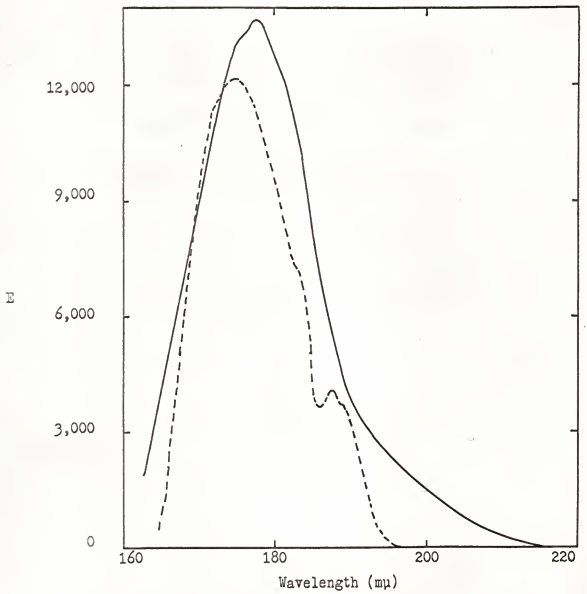


Figure 13.—Ultraviolet absorption in the gas phase of V1 (solid line) and V1C (broken line).

The spectroscopic data obtained afford the following main observations:

(i) V2C absorbed at a shorter wavelength than V1C in solution, at longer wavelength than V1C (main peak) in the gas phase.
(ii) Change in solvent from heptane to acetonitrile affected V2C much more than V1C, so that the shift between the two compounds was greatly reduced.
(iii) The V2C extinction coefficient was much short of additivity with respect to V1C, but observation of the spectra showed that the area under the V2C spectrum was much broader than the corresponding V1C area.
(iv) The shoulders observed for the two compounds in the gas phase did not seem to be related.

Discussion of the Vinylmethylsilane Carbon Analogues Study

A contradiction in the relative position of the absorption maxima of V1C and V2C in solution and in the gas phase was observed. This contradiction ceases to exist when one considers that solution bands represent the average of various independent peaks, which can often be observed in the gas phase. It is therefore proposed that the true absorption maximum of V1C is the one of the main peak observed in the gas phase (Table 26, Figure 13); the V2C absorption shows therefore a bathochromic shift over V1C of 1.7 mμ.

Strong hyperconjugative effects should be present in V1C, and even stronger in V2C, where two unconjugated double bonds are present. This would explain the V2C-V1C bathochromic shift, and would also explain why the bathochromic effect caused by the change in solvent from non-polar to polar affected V2C much more than V1C. The gas phase spectrum of V1C showed two peaks, while only one was observed for V2C; this could be due to the different geometry of the two molecules: one additional transition could be allowed to the asymmetrical V1C structure, forbidden to the symmetrical V2C structure. The shoulders observed for

both compounds could have been caused by vibrational interactions, similar to the ones discussed for A1C and A2C.

The spectra obtained for the carbon analogues of the vinylsilanes were widely different from the spectra of the vinylsilanes themselves (see for example Figure 13) in shape and behavior. This is most likely due to the hyperconjugative effects of the methyl groups, missing in the vinylsilanes, where the silicon atom acts as an effective insulator. The vinylsilanes absorbed at a wavelength only slightly longer (average shift: 0.5 mμ) than the carbon analogues; possibly the hyperconjugative effects present in the carbon compounds are as effective as the silicon atom interaction in lowering the energy of the excited state.

In conclusion, (i) the difference in ultraviolet behavior between vinylsilanes and carbon analogues shows that silicon interaction is undoubtedly present in the vinylsilanes; (ii) the difference in ultraviolet behavior between the carbon analogues of vinylsilanes and the carbon analogues of allylsilanes shows that additional forces must be at work in the allylsilanes.

CHAPTER V

RESULTS AND DISCUSSION OF THE ALLYLPROPYLSILANES STUDY

Spectroscopic Data

The ultraviolet absorption of isooctane and 95 per cent ethanol solutions of allyltripropylsilane (A1P), diallyldipropylsilane (A2P), and triallylpropylsilane (A3P) (all known compounds) was determined. The spectroscopic data are shown in Tables 28 to 31; tetraallylsilane (A4) values have been included for comparison. The compounds absorbed in the 190-200 mμ region, with extinction coefficients ranging from 10,000 to 30,000. Absorbance was plotted *vs.* molarity for four concentrations to check the adherence to Beer's law (Figures 14 and 15): good adherence was obtained for both solvents. The low vapor pressure of allylpropylsilanes did not allow any gas phase determinations.

TABLE 28

λ_{max} AVERAGES OF ALLYLPROPYLSILANES (ISOOCTANE SOLUTIONS)

Compound	λ_{max} Average (mμ)	Departures from Average	Shift Average (mμ)	Shift Additivity (A2P-A1P shift set at 1)
A1P	194.5	± 0.2%	1.3	1.00
A2P	195.8	± 0.2%	0.6	0.46
A3P	196.4	± 0.1%	0.3	0.23
A4[a]	196.7	-		

[a]This spectrum was obtained at the same time as the allylpropylsilanes. Deviation from Table 3: + 0.25%.

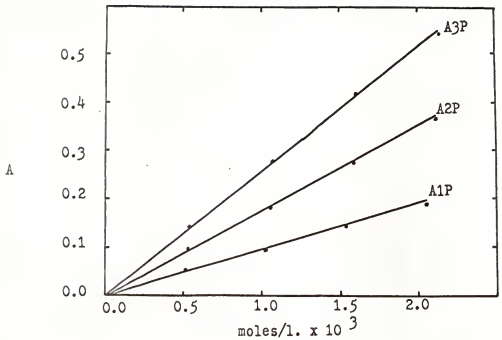


Figure 14.—Adherence to Beer's law of allylpropylsilanes (isooctane solutions.

TABLE 29

EXTINCTION COEFFICIENT AVERAGES OF ALLYLPROPYLSILANES (ISOOCTANE SOLUTIONS)

Compound	E Average	Departures from Average	Additivity (E_{A1P} set at 1)
A1P	10,129	± 5%	1.0
A2P	18,626	± 5%	1.8
A3P	27,343	± 4%	2.7
A4[a]	37,271	± 6%	3.7

[a]From Table 4.

TABLE 30

λ_{max} AVERAGES OF ALLYLPROPYLSILANES (ETHANOL SOLUTIONS)

Compound	λ_{max} Average (mμ)	Departures from Average	Shift Average (mμ)	Shift Additivity (A2P-A1P shift set at 1)
A1P	194.9	± 0.1%		
			1.3	1.00
A2P	196.2	± 0.0%		
			0.8	0.61
A3P	197.0	± 0.0%		
			0.4	0.31
A4[a]	197.4	-		

[a]This spectrum was obtained at the same time as the allylpropylsilanes. Deviation from Table 6: + 0.2%.

TABLE 31

EXTINCTION COEFFICIENT AVERAGES OF ALLYLPROPYLSILANES (ETHANOL SOLUTIONS)

Compound	E Average	Departures from Average	Additivity (E_{A1P} set at 1)
A1P	9,670	± 6%	1.0
A2P	17,715	± 4%	1.8
A3P	26,347	± 3%	2.7
A4[a]	35,954	± 2%	3.7

[a]From Table 7.

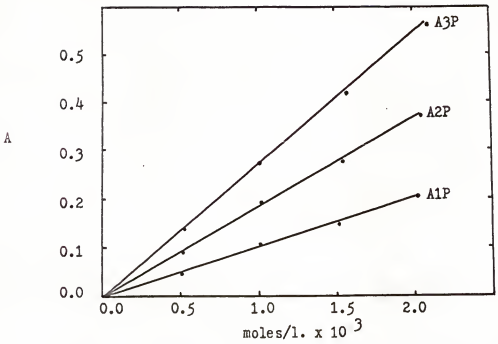


Figure 15.—Adherence to Beer's law of allylpropylsilanes (ethanol solutions).

Observation of the spectroscopic data obtained shows that for both nonpolar and polar solutions, increasing the degree of allyl substitution:

(i) A progressive bathocromic shift occurs.
(ii) The bathochromic shifts decrease asymptotically.
(iii) The extinction coefficiants increase progressively, but remain 10 per cent short of straight additivity.

With a change in solvent from isooctane to 95 per cent ethanol, the bathochromic shifts and hypochromic effects observed showed almost no change with increasing allyl substitution (hypochromic effects in brackets):

A1P	0.4 mμ	(4.5%)
A2P	0.4 mμ	(4.9%)
A3P	0.4 mμ	(3.6%)

Discussion

The spectroscopic data obtained for the allylpropylsilanes, such as the asymptotically decreasing bathochromic shifts, and the numerical values of the extinction coefficients, show a very close similarity to the spectroscopic data obtained for the allylmethylsilanes (Chapter II). No structure effects could be present in the allylpropylsilanes, where the only change occurring with increasing allyl substitution is the removal of two hydrogens; it would therefore appear that structure effects are excluded as a sole possible cause of the bathochromic shifts observed in the allylmethylsilane series.

Structure effects of inductive nature, however, are responsible for the fact that the allylpropylsilanes absorbed at a longer wavelength than the allylmethylsilanes, with AP-A shifts progressively decreasing with increasing allyl substitution (average shifts: 1.7, 0.9, 0.6 mμ), as expected from the decrease in amount of structure change occurring; inductive effects must therefore be contributing to the bathochromic shifts observed in the allylmethylsilane series. Their total amount of contribution should be given by the difference in maximum total shift tetraallyl-monoallyl obtained for the two series (allylmethylsilanes, 3.9 mμ; allylpropylsilanes, 2.5 mμ), namely 1.4 mμ.

Steric effects in the allylpropylsilane series should also be considered; however, these effects appear contradictory. Propyl groups would be expected to increase the ease of formation of the conjugative structures shown in Chapter II; however, the molecular motions of the propyl groups would be expected to reduce the stability of the same structures. Steric acceleration in cyclopolymerization (which was shown

in Chapter II to be related to the interactions observed) has not yet been established; when t-butyldiallylamine and diallylamine were cyclopolymerized under the same conditions, saturated intra-intermolecular cyclic polymers were obtained from both monomers.[3]

In the allylmethylsilane series, with a change in solvent from isooctane to 95 per cent ethanol, the bathochromic shift and hypochromic effect observed were more pronounced for allyltrimethylsilane than for the other allylmethylsilanes; as a consequence, the total bathochromic shift A4-A1 was decreased, and the extinction coefficient ratios reached additivity. In the allylpropylsilane series, on the contrary, the bathochromic shift and hypochromic effect observed for A1P with a change in solvent from isooctane to 95 per cent ethanol were nearly the same as the ones obtained for the other allylpropylsilanes; as a consequence, the total bathochromic shift A4-A1P was not decreased (it actually increased slightly) and the extinction coefficient ratios remained unchanged. It is suggested that the difference in behavior is due to steric hindrance to solvation in the allylpropylsilane series; this hindrance should be at its maximum in A1P, which differs the most from its methyl analogue A1. Propyl groups would greatly hinder the formation of solvated complexes such as XII (Chapter II).

CHAPTER VI

RESULTS AND DISCUSSION OF THE ALLYLDIMETHYLVINYLSILANE STUDY

Spectroscopic Data

The ultraviolet absorption of heptane and acetonitrile solutions of allyldimethylvinylsilane (AV), a new product previously synthesized in this laboratory by R. W. Stackman,[70] was determined. The spectroscopic data are reported in Table 32; the table includes absorption

TABLE 32

SPECTROSCOPIC DATA OF ALLYLDIMETHYLVINYLSILANE

Absorption	Phase	λ_{max} Average (mμ)	Departures from Average	E Average	Departures from Average
AV peak	heptane solution	177.4	± 0.1%	20,433	± 1%
AV peak	acetonitrile solution	177.7	± 0.5%	18,395	± 3%
AV peak	gas	178.2	-	-	-
AV shoulder	heptane solution	193.9	± 0.3%	14,974	± 3%
AV shoulder	acetonitrile solution	193.9	± 0.2%	13,817	± 4%
AV shoulder	gas	190.8	-	-	-

maxima obtained in the gas phase (the low vapor pressure of the compound did not allow a determination of the extinction coefficients). The

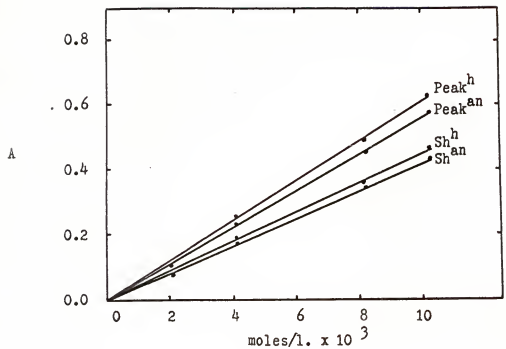


Figure 16.—Adherence to Beer's law of allyldimethylvinylsilane (solution spectra).

^{h}heptane

^{an}acetonitrile

^{Sh}shoulder

absorbance of solution spectra was plotted vs. molarity for four concentrations to check the adherence to Beer's law (Figure 16): good adherence was obtained.

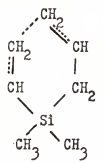
The ultraviolet absorption of the compound showed for all media a peak in the 177-178 mμ region and a shoulder in the 190-194 mμ region, with extinction coefficients ranging around 19,000 and 14,000 respectively. The flat contour of the shoulder did not allow a very accurate λ_{max} determination.

A small bathochromic shift (at least for the peak value) and a hypochromic effect was observed with a change in solvent from heptane to

acetonitrile. The absorbance in the gas phase showed a hypsochromic shift over solution spectra for the shoulder, but a slight bathochromic shift for the peak value.

Discussion

AV scale models show that any interaction of the intra-intermolecular type (terminal carbon atom of one double bond interacting with the inside carbon atom of the other double bond) is highly strained, and very unlikely; attempts by Stackman[70] to cyclopolymerize the material were not successful. Alternate structures such as XXV appear also unlikely, due to the reduced capacity of charge stabilization.



XXV

These conclusions are supported by the AV ultraviolet spectrum, which showed two independent absorptions, one in the vinylsilane region and one in the allylsilane region. Particularly significant is the fact that two absorptions were present both in the gas phase and in solution, eliminating vibronic interactions as a possible cause of the shoulder. Interaction between the two unconjugated double bonds would have been expected to give one peak only or, at any rate, a spectrum different from the original components.

CHAPTER VII

CONCLUSIONS

The progressive bathochromic shifts observed for the allylmethylsilane series could not be due to silicon d orbital participation because a bathochromic wavelength shift was observed between the first two carbon analogues of the allylmethylsilanes. They could not be due solely to structure effects from progressive replacement of methyl with allyl groups because progressive bathochromic shifts were observed for the allylpropylsilane series, where no structure changes occur.

Silicon interaction is present because the allylmethylsilanes absorbed at a longer wavelength (average shift: 10 mμ) than the carbon analogues; this interaction appears to affect all the allylmethylsilanes in equal amount. Structure effects are present because the maximum total shift tetraallyl-monoallyl observed for the allylpropylsilane series (2.5 mμ) was smaller than the one observed for the allylmethylsilane series (3.9 mμ).

It is proposed that the progressive bathochromic shifts observed for the allylmethylsilane series are due to a homoconjugative interspatial interaction between the double bonds, leading to pseudo-butadiene, pseudo-hexatriene, and pseudo-octatetraene structures. The conjugative character of the interaction is shown by similarity in the behavior of the spectroscopic data of allylsilane series and conjugated polyene

series. Furthermore, vinylmethylsilanes, where such structures could not be drawn, did not show any bathochromic shifts with increasing vinyl substitution; allyldimethylvinylsilane, where a pseudo-conjugative structure is highly unlikely, showed independent allyl and vinyl absorptions. The conjugative character of the interaction is also supported by a linear relationship between absorption frequencies and HMO Δm values for the pseudo-conjugated structures postulated (k [partial bond] : 0.6β), and by very close numerical values for the frequency shift ratios and the $\Delta\Delta m$ ratios.

It is found that the structures drawn for the ultraviolet excited state of the allylsilanes coincide with the structures postulated for the transition state of intra-intermolecular cyclopolymerization. All the polyallylmethylsilanes studied have been cyclopolymerized to soluble polymers, and kinetic studies on the free-radical polymerization of allylmethylsilanes gave activation energy ratios close in numerical value to the shift ratios obtained from the ultraviolet study.

CHAPTER VIII

EXPERIMENTAL

Equipment and Data

Temperatures reported are uncorrected and in degrees centigrade.

Refractive indices were determined with a Bausch & Lomb Abbe 34 Refractometer equipped with an achromatic compensating prism.

Vapor phase chromatographic (VPC) analyses were carried out with an F & M Model 700 Laboratory Chromatograph using helium as effluent gas and a fifteen-foot 20 per cent FFAP* column and/or an eight-foot 10 per cent diisodecylphthalate column.

Infrared spectra were obtained with a Perkin-Elmer Infracord Infrared Recording Spectrophotometer; the infrared absorption values are reported in microns.

Nuclear magnetic resonance (NMR) spectra were obtained with a Varian V-4302 High Resolution Nuclear Magnetic Resonance Spectrometer.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

All reagents used were distilled, reagent grade, products.

Ultraviolet spectra were obtained with a nitrogen flushed Beckman Model DK-2A Ratio Recording Spectrophotometer equipped with far ultraviolet silica optics and cells. Wavelengths were calibrated with mercury emission lines. Experimental details are given in the next section.

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Experimental Procedures in the Ultraviolet Study

Nitrogen purge.—A nitrogen purge of 1.5 cu.ft./min. was used below 190 mμ; of 0.3 cu.ft./min. between 190 and 210 mμ.

Solution spectra.—The path lengths and concentrations used are reported in Table 33. When series of compounds were studied (e.g. A1, A2, A3, A4), series of spectra having the same concentration were obtained on the same sheet of chart paper.

TABLE 33

PATH LENGTHS AND CONCENTRATIONS USED IN THE ULTRAVIOLET STUDY

Absorption	Path Length (mm)	Molarity
Above 190 mμ	0.10	0.5×10^{-3}
	0.10	1.0×10^{-3}
	0.10	1.5×10^{-3}
	0.10	2.0×10^{-3}
	0.03	1.0×10^{-2}
Below 190 mμ	0.03	2.0×10^{-3}
	0.03	4.0×10^{-3}
	0.03	6.0×10^{-3}
	0.03	8.0×10^{-3}
	0.03	1.0×10^{-2}

Gas phase spectra.—Pressures, ranging between 1 and 15 mm., were measured with a Dubrovin gauge (Welch Scientific Company), at constant temperature (20°). Molarities were obtained from the formula $M = \frac{P}{RT}$ (from the gas law, $PV = nRT$; $M = \frac{n}{V}$) where P is pressure in

atmospheres, or $\frac{mm.}{760}$, R = 8.205 x 10^{-2} l.atm./mole deg. and T = ^{o}K. Two sets of matched cells were available, of 1 and 10 mm. path length. The 1 mm. cells allowed quantitative determinations (λ_{max} and extinction coefficients) of compounds boiling up to 100°. The 10 mm. cells allowed qualitative determinations (λ_{max} only) of compounds boiling up to 180°, because the low pressures to be used could not be measured accurately. Where quantitative determinations were possible, spectra of the same compound, at four different pressures (e.g. 2, 4, 6, 8 mm.), were obtained on the same sheet of chart paper; the λ_{max} value reported was the one of the sharpest peak obtained (highest pressure); to test the pressure measurement, two or more spectra with newly filled cells were run for each pressure value.

Solvents.—Solvents were used as received. Spectral grades were used for isooctane (Fisher Scientific Co.), heptane (Fisher Scientific Co.), acetonitrile (Eastman Organic Chemicals); technical grade for 95 per cent ethanol (Union Carbide).

Materials.—All the compounds studied were redistilled materials, gas-chromatographically pure. The available amount of 3,3-dimethyl-1,4-pentadiene did not allow distillation of the material; VPC analysis showed that the product was 95 per cent pure: the product was used as such, then a small amount was brought to 100 per cent purity by preparative chromatography;* a gas phase spectrum of the 100 per cent purity material was found identical to the gas phase spectra obtained with the 95 per cent purity material.

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*Aerograph Autoprep Model A 700, Wilkens Instruments & Research, Inc.; eight-foot 20 per cent FFAP column.

Source of Materials Commercially Available

Allyltrimethylsilane, diallyldimethylsilane, trimethylvinylsilane, dimethyldivinylsilane, and tetravinylsilane were obtained from Peninsular ChemRsearch, Inc.; 3,3-dimethyl-1-butene and 4,4-dimethyl-1-pentene were obtained from Columbia Organic Chemicals.

Synthesis of Known Compounds Not Commercially Available

Allylmagnesium Bromide.—In a 5 l. three-necked flask previously flamed out and flushed with nitrogen (a nitrogen static pressure was maintained throughout the preparation), fitted with stirrer, reflux condenser, and addition funnel, was placed 146 g. (6 g. atoms) of magnesium turnings and 3 l. of dry ether. Stirring was started, then a few mls. of allyl bromide out of a total of 364 g. (3 moles) was added; when the ether began to reflux, the flask was cooled with an ice-bath, and the remainder of the allyl bromide, diluted with an equal volume of ether, was added dropwise over a period of 10.5 hours. When the addition was completed, the flask was stirred for one additional hour at r. t., then the yellow-grey solution was decanted through a glass wool plug. Yield (determined by titration): 78 per cent.

Triallylmethylsilane.—In a 2 l. three-necked flask previously flamed out and flushed with nitrogen (a nitrogen static pressure was maintained throughout the preparation), fitted with stirrer, reflux condenser, and addition funnel, was placed 1360 ml. of 0.71 N ether solution (0.966 mole) of allylmagnesium bromide; stirring was started, then 50 g. (0.322 mole) of allylmethyldichlorosilane (Peninsular ChemRsearch, Inc.) was added rapidly, dropwise. A slightly exothermic reaction occurred; a white precipitate started to form near the end of the

addition. Ether was distilled off through a water aspirator until a temperature of 60° was reached (incipient evolution of white smokes), then 300 ml. of dry benzene was added, and stirring and refluxing was continued for 12 hours. The reaction mixture was then cooled with an ice-bath, and hydrolyzed by cautious addition of 1 N hydrochloric acid until acidic reaction was obtained. The organic layer plus one ether extract were washed with water, then dried over anhydrous magnesium sulfate. After removal of the solvent, fractionation gave 27.4 g. (51.2%) of triallylmethylsilane. After two further fractionations, 7.9 g. of VPC pure product b.p. 62.5° (10 mm.), n_D^{20} 1.4669 (reported:[49] b.p. 180.3°, n_D^{20} 1.4662) was obtained.

Tetraallylsilane.—The product was obtained using the same procedure outlined for triallylmethylsilane from 0.828 mole of allylmagnesium bromide and 50 g. (0.276 mole) of diallyldichlorosilane (Peninsular ChemRsearch, Inc.). One fractionation gave 41.3 g. (78.0%) of tetraallylsilane; after two further fractionations, 15.6 g. of VPC pure product b.p. 54.5° (1 mm.), n_D^{20} 1.4864 reported:[24] b.p. 102-103° (15 mm.), n_D^{20} 1.4864) was obtained.

Methyltrivinylsilane.—In a 1 l. three-necked flask previously flamed out and flushed with nitrogen (a nitrogen static pressure was maintained throughout the preparation), fitted with stirrer, reflux condenser, and addition funnel, was placed 333 ml. of 3.0 M tetrahydrofuran solution (1.0 mole) of vinylmagnesium chloride (Peninsular ChemResearch, Inc.), then 46.5 g. (0.33 mole) of vinylmethyldichlorosilane (Peninsular ChemResearch, Inc.) in 50 ml. of dry tetrahydrofuran was added dropwise, with stirring, over a three-hour period. On addition, a slightly exothermic reaction was observed, and the reaction mixture became fairly

viscous. After further stirring at r.t. for two hours, the reaction mixture was cooled with an ice-bath, and hydrolyzed by dropwise addition of 1 N hydrochloric acid until acidic reaction was obtained. The organic layer plus one ether extract were washed with water, then dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, fractionation gave 13.4 g. (32.7%) of methyltrivinylsilane. Refractionation gave 8.2 g. of VPC pure product, b.p. 49.5° (100 mm.), n_D^{20} 1.4422 (reported:[71] b.p. 107.6°, n_D^{25} 1.4411).

Allyltripropylsilane.—In a 1 l. three-necked flask previously flamed out and flushed with nitrogen (a nitrogen static pressure was maintained throughout the preparation), fitted with stirrer, reflux condenser, and addition funnel, was placed 500 ml. of 0.74 N ether solution (0.362 mole) of allylmagnesium bromide, then 46.5 g. (0.241 mole) of tripropylchlorosilane (Peninsular ChemRsearch, Inc.) in 50 ml. of dry ether was added dropwise, with stirring, over a 40 minute period. A mild exothermic reaction was observed, and a precipitate formed. After further six hours of stirring at r.t. the reaction mixture was hydrolyzed by pouring over cracked ice and 1 N hydrochloric acid. The organic layer plus one ether extract were washed with saturated salt solution and dried over anhydrous magnesium sulfate. After removal of the solvent, fractionation gave 37.9 g. (79.4%) of allyltripropylsilane. After refractionation, 27.8 g. of VPC pure product b.p. 86.5-86.8° (9 mm.), n_D^{20} 1.4492 (reported:[72] b.p. 217°, n_D^{20} 1.4490) was obtained.

Triallylpropylsilane.—The product was obtained using the same procedure outlined for allyltripropylsilane from 1.92 mole of allylmagnesium bromide and 75.9 g. (0.427 mole) of propyltrichlorosilane

(Peninsular ChemRsearch). A two-hour addition time was required, due to the occurrence of an exothermic reaction. Fractionation gave 66.8 g. (80.0%) of triallylpropylsilane; on refractionation, 60.0 g. of VPC pure product b.p. 86° (9 mm.), n_D^{20} 1.4728 (reported:[72] b.p. 218.3°, n_D^{20} 1.4705) was obtained. The infrared spectrum (values identical with the ones reported for diallyldipropylsilane) confirmed the synthesis of the material.

n-Propyl lithium.[74]—In a 500 ml. three-necked flask previously flamed out and flushed with nitrogen (a nitrogen static pressure was maintained throughout the preparation), fitted with stirrer, low temperature thermometer, and addition funnel, was placed 250 ml. of dry ether, then 11.1 g. (1.6 g. atom) of lithium wire was cut into the flask. Stirring was started, then about forty drops of a solution of 80.0 g. (0.65 mole) of 1-bromopropane (Eastman Organic Chemicals) in 75 ml. of ether was added; the flask was cooled to -10° with a dry ice-isopropanol bath as soon as the reaction started, and kept at that temperature during the addition of the remainder of the 1-bromopropane solution (40 minutes). When the addition was completed, the reaction mixture was slowly warmed up to r.t. over 2.5 hours, then decanted through a glass wool plug. Yield (determined by titration): 97.5 per cent.

Diallyldipropylsilane.—The experimental procedure followed for the other allylpropylsilanes gave only an impure product when applied to diallyldipropylsilane; a pure product was obtained as follows. In a 1 l. three-necked flask previously flamed out and flushed with nitrogen (a nitrogen static pressure was maintained throughout the preparation), fitted with stirrer, reflux condenser, and addition funnel, was placed

a n-propyl lithium solution prepared from 7.8 g. (1.13 g. atom) of lithium in 200 ml. of ether and 56.5 g. (0.46 mole) of 1-bromopropane in 100 ml. of ether. The n-propyl lithium solution was diluted with 200 ml. of ether, then 28.7 g. (0.158 mole) of carefully fractionated (b.p. 81° [50 mm.]) diallyldichlorosilane (Peninsular ChemResearch, Inc.) was added dropwise, with stirring, over a 1.5 hour period, while cooling with a salt-ice bath. After further stirring and cooling for 20 minutes, the reaction mixture (containing a white precipitate) was poured over cracked ice and 150 ml. of 1 N hydrochloric acid. The organic layer plus one ether extract were washed with saturated salt solution, then dried over anhydrous magnesium sulfate. After removal of the solvent by distillation, fractionation gave 6.2 g. (20.0%) of VPC pure diallyldipropylsilane, b.p. 89° (10 mm.), n_D^{20} 1.4598, d_4^{20} 0.8050 (reported:[73] b.p. 76-78° [2 mm.], n_D^{20} 1.4555, d_4^{20} 0.8050). Due to the discrepancy in the refractive index, the synthesis of the compound was confirmed by elemental analysis and infrared spectrum. Infrared spectrum: absorptions at 3.23, 3.38 (CH_2=); 3.40, 6.92 (CH_2-); 3.47, 7.23 (CH_3-); 6.18, 7.10, 10.12, 11.20 (vinyl); 6.88 (n-propyl); 8.70, 12.25, 12.80 (Si-C); 8.35, 9.40 (Si-C ?); 7.55, 10.76 (unidentified).

Anal. Calcd. for $C_{12}H_{24}Si$: C, 73.38; H, 12.32; Si, 14.30. Found: C, 73.58; H, 11.94, Si, 14.33.

3,3-Dimethyl-1,4-pentadiene.—The product had been previously prepared in this laboratory by R. B. Kasat, following an established procedure.[75]

Allyldimethylvinylsilane.—This previously unreported product had been obtained by R. W. Stackman[70] in this laboratory using the same procedure outlined for methyltrivinylsilane.

Synthesis of 4,4-Dimethyl-1,6-heptadiene

Propionaldehyde diallyl acetal.—In a screw-cap gallon bottle was placed 1072 g. (18.4 moles) of allyl alcohol (Eastman Organic Chemicals) and 444 g. (4moles) of anhydrous calcium chloride (Fisher Scientific Co.). The mixture was cooled to 5° with a salt-ice bath, shaking frequently, then 465 g. (8 moles) of propionaldehyde (Eastman Organic Chemicals) was slowly added down the sides of the bottle so as to form a layer on the alcoholic calcium chloride. The bottle was then sealed with the screw-cap and shaken; an exothermic reaction took place. After occasional shaking at r.t. for two days, enough water to dissolve the calcium chloride was added, then the upper layer was washed four times with large amounts of water, and dried over anhydrous magnesium sulfate. Fractionation (under nitrogen, cuprous chloride added) gave 852 g. (68.2%) of propionaldehyde diallyl acetal (a new product), b.p. 81.5° (43 mm.), n_D^{20} 1.4277, d_4^{20} 0.8713. Infrared spectrum: absorptions at 3.25, 3.36 (CH_2=); 3.41 (CH_2-); 3.50, 6.85, 7.25 (CH_3-); 6.08, 7.09, 9.20, 10.05, 10.90 (vinyl); 8.75 (C-O); 9.6 (weak, unidentified).

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.27; H, 10.32.

2-Methyl-4-pentenal.—In a 2 l. three-necked flask fitted with a thermometer with Therm-O-Watch* electronic temperature controller, addition funnel, gas inlet, and a one-foot vacuum-jacketed column packed with Raschig rings and topped by a still-head, was placed 500 g. of dibutyl sebacate and a trace of cuprous chloride. A stream of nitrogen was started, then the dibutyl sebacate was heated to 210° and kept at that temperature while 850 g. (5.44 moles) of propionaldehyde diallyl

*I^2R Instruments, Inc., Cheltenham, Pennsylvania.

acetal was added dropwise, over a nine-hour period. Distillate was collected during this time, at a temperature ranging from 85 to 120°. After the addition was completed, the temperature was raised to 260° to collect all the product. The distillate (823 g.) was washed with water to remove the allyl alcohol present, then dried over anhydrous magnesium sulfate. Fractionation (under nitrogen, cuprous chloride added) gave a series of fractions found by VPC to have the following composition: recovered propionaldehyde diallyl acetal: 241.4 g. (28.4%); 2-methyl-4-pentenal: 257.9 g. (48.3%); 2-allyl-2-methyl-4-pentenal, 3.1 g. (2.2%). Refractionation of the fractions b.p. 117-120° gave 94.8 g. of pure 2-methyl-4-pentenal (a new product*), b.p. 118-118.5°, n_D^{20} 1.4204, d_4^{20} 0.8397. Infrared spectrum: absorptions at 3.32, 3.36, 3.52 (CH_2=); 3.41, 6.89 (CH_2-); 3.69 (aliphatic aldehyde); 5.80 (C=O); 6.08, 7.04, 7.10, 10.05, 10.90 (vinyl); 7.28 (CH_3-).

Anal. Calcd. for $C_6H_{10}O$: C, 73.42; H, 10.27. Found: C, 73.10; H, 10.38.

2,4-Dinitrophenylhydrazone: m.p. 101-102°. Anal. Calcd. for $C_{12}H_{14}N_4O_4$: C, 51.79; H, 5.07; N, 20.13. Found: C, 51.56; H, 5.36; N, 20.13.

2-Methyl-4-pentenal diallyl acetal.—The product was obtained using the same procedure outlined for propionaldehyde diallyl acetal from 129 g. (2.22 moles) of allyl alcohol, 53.7 g. (0.483 mole) of anhydrous calcium chloride, and 94.8 g. (0.965 mole) of 2-methyl-4-pentenal. Fractionation (under nitrogen, cuprous chloride added) gave 119.5 g. (63.1%) of 2-methyl-4-pentenal diallyl acetal (a new product), b.p. 99° (19 mm.), n_D^{20} 1.4456, d_4^{20} 0.8797. Infrared spectrum: absorptions

*The compound is mentioned in a Russian abstract[76] among the products obtained from alkali cleavage of diallylammonium salts, but no physical constants are given.

at 3.25, 3.36 (CH_2=); 3.41, 6.98 (CH_2-); 3.50, 6.85, 7.18 (CH_3-); 6.08, 7.06, 9.25, 10.05, 10.80 (vinyl); 8.98 (C-O); 7.35, 7.88 (unidentified).

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 74.28; H, 10.37.

2-Allyl-2-methyl-4-pentenal.—The product was obtained using the same procedure outlined for 2-methyl-4-pentenal, but dibutyl phthalate (120 g.) was used instead of dibutyl sebacate. 2-Methyl-4-pentenal diallyl acetal (115 g., 0.52 mole) gave in two hours 92 g. of distillate, b.p. 95-166°. After one fractionation, 47.4 g. (66.0%) of 2-allyl-2-methyl-4-pentenal (a new product) was obtained; refractionation gave 36.4 g. of pure product, b.p. 58° (12 mm.), n_D^{20} 1.4482, d_4^{20} 0.8597. Infrared spectrum: absorptions at 3.22, 3.36, 3.52 (CH_2=); 3.41, 6.89 (CH_2-); 3.69 (aliphatic aldehyde); 5.80 (C=O); 6.08, 7.04, 7.10, 10.05, 10.90 (vinyl); 7.28 (CH_3-); 11.40, 11.65 (weak, unidentified).

Anal. Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.60; H, 10.24.

2,4-Dinitrophenylhydrazone: m.p. 115-116°. Anal. Calcd. for $C_{15}H_{18}N_4O_4$: C, 56.59; H, 5.70; N, 17.60. Found: C, 56.14; H, 5.62; N, 17.46.

4,4-Dimethyl-1,6-heptadiene.—In a 1 l. three-necked flask fitted with a thermometer and a reflux condenser was placed 350 ml. of diethylene glycol, 47.0 g. (0.84 mole) of potassium hydroxide, 36.4 g. (0.262 mole) of 2-allyl-2-methyl-4-pentenal, and 35.5 ml. of 85 per cent hydrazine hydrate (0.622 mole) (Fisher Scientific Co., purified grade). The reaction mixture was refluxed for 1.5 hour (at which time the reaction

temperature did not show any further decrease due to the production of water), then a Dean-Stark trap was interposed between flask and reflux condenser, and aqueous liquor was removed until the reaction temperature reached 190°. The reaction mixture was then refluxed for four hours, during which time small amounts of aqueous liquor had to be removed to keep the temperature at 185-190°. After cooling to r.t., the organic layer from the trap plus three ether extracts of the combined aqueous layer and reaction mixture were washed with water until neutral, then dried over anhydrous magnesium sulfate. After removal of the solvent, fractionation gave 24.9 g. (76.5%) of VPC pure 4,4-dimethyl-1,6-heptadiene (a new product), b.p. 63° (90 mm.), n_D^{20} 1.4283, d_4^{20} 0.7427. Infrared spectrum: absorptions at 3.21, 3.35 (CH_2=); 3.42, 6.83 (CH_2-); 5.48 (vinyl overtone); 6.11, 10.05, 10.95 (vinyl); 6.98, 7.10 (CH_3-); 7.23, 7.34 (gem-dimethyl); 8.48, 11.18, 13.05 (weak, unidentified). The NMR spectrum showed two multiplets centered at about 4.13 τ (-CH=) and 5.00 τ (CH_2=), a doublet centered at 8.07 ($-CH_2-$), and a singlet at 9.13τ(CH_3-); the areas were 0.9/2.3/2.2/3.0 respectively.

Anal. Calcd. for C_9H_{16}: C, 87.01; H, 12.98. Found: C, 87.19; H, 12.83.

CHAPTER IX

SUMMARY

Far ultraviolet spectra of sixteen compounds containing unconjugated double bonds were determined. Progressive bathochromic wavelength shifts were observed within the following series of compounds: (i) allyltrimethylsilane, diallyldimethylsilane, triallylmethylsilane, tetraallylsilane; (ii) 4,4-dimethyl-1-pentene, 4,4-dimethyl-1,6-heptadiene; (iii) allyltripropylsilane, diallyldipropylsilane, triallylpropylsilane. In the series trimethylvinylsilane, dimethyldivinylsilane, methyltrivinylsilane, and tetravinylsilane, trimethylvinylsilane was shifted bathochromically from the rest of the vinylsilanes, which were grouped together. 3,3-Dimethyl-1,4-pentadiene was shifted bathochromically from 3,3-dimethyl-1-butene in the gas phase, hypsochromically in solution. Allyldimethylvinylsilane showed two independent absorptions.

A homoconjugative interspatial interaction is postulated as cause of the progressive bathochromic shifts observed for the allylmethylsilane series. Two possible alternate causes, namely an interaction with the silicon atom and structure effects due to the progressive replacement of methyl with allyl groups, are excluded by the spectroscopic results obtained for series (ii) (carbon analogues of the allylmethylsilanes) and series (iii) (propyl analogues of the allylmethylsilanes). Structures depicting the interspatial conjugative interaction have been drawn; the vinylsilane series, for which no such

structures could be drawn, did not show progressive bathochromic shifts; allyldimethylvinylsilane, to which such structures are unlikely to apply, showed independent allyl and vinyl absorptions. The conjugative character of the interaction is also supported by a linear relationship between absorption frequencies and HMO Δm values for the pseudo-conjugated structures postulated for the allylmethylsilanes, and by close similarity between shift ratios and $\Delta\Delta m$ ratios.

It is found that the structures drawn for the ultraviolet excited state of the allylsilanes coincide with the structures postulated for the transition state of intra-intermolecular cyclopolymerization. The identity is supported by close similarity between the activation energy ratios for the free radical polymerization of allylmethylsilanes and the shift ratios from the ultraviolet study.

BIBLIOGRAPHY

1. J. R. Dyer, Applications of Absorption Spectroscopy of Organic Compounds, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p. 9.

2. H. H. Jaffe and M. Orchin, Theory and Applications of Ultraviolet Spectroscopy, J. Wiley and Sons, Inc., New York, N. Y., 1962.

3. G. B. Butler, J. Polymer Sci., 48, 279 (1960).

4. E. A. Braude, J. Chem. Soc., 1902 (1949).

5. L. Bateman and G. A. Jeffrey, Nature, 152, 446 (1943).

6. G. A. Jeffrey, Proc. Roy. Soc., A183, 388 (1945).

7. N. J. Leonard, Record Chem. Progr., 17, 243 (1956).

8. N. J. Leonard and F. H. Owens, J. Am. Chem. Soc., 80, 6039 (1958).

9. S. Winstein, L. De Vries, and R. F. Orloski, J. Am. Chem. Soc., 83, 2020 (1961).

10. R. F. Orloski, Ph. D. Dissertation, University of California, Los Angeles, August, 1963.

11. G. B. Butler and R. J. Angelo, J. Am. Chem. Soc., 79, 3128 (1957).

12. G. B. Butler, A. Crawshaw and W. L. Miller, J. Am. Chem. Soc., 80, 3615 (1958).

13. T. F. Gray, Ph. D. Dissertation, University of Florida, December, 1964.

14. C. S. Marvel and W. E. Garrison, J. Am. Chem. Soc., 81, 4737 (1959).

15. G. B. Butler and T. W. Brooks, J. Org. Chem., 28, 2699 (1963).

16. R. B. Woodward, J. Am. Chem. Soc., 63, 1123 (1941); 64, 72, 76 (1942).

17. G. B. Butler and M. A. Raymond, J. Org. Chem., 30, 2410 (1965).

18. M. A. Raymond, Ph. D. Dissertation, University of Florida, December, 1962.

19. J. J. van Heinigen, Unpublished Work.

20. L. E. Ball, Ph. D. Dissertation, University of Akron, June, 1961.

21. G. B. Butler and R. W. Stackman, J. Org. Chem., 25, 1643 (1960).

22. C. S. Marvel and R. G. Woolford, J. Org. Chem., 25, 1641 (1960).

23. D. S. Trifan and J. J. Hoglen, J. Am. Chem. Soc., 83, 2021 (1961).

24. E. L. Kropa, U. S. Patent 2,388,161; Oct. 30, 1945.

25. N. S. Bayliss and E. G. McRae, J. Phys, Chem., 58, 1002, 1006 (1954).

26. A. Burawoy, Ber., 63, 3155 (1930).

27. A. Burawoy, J. Chem. Soc., 1177 (1939).

28. R. S. Mulliken, Revs. Modern Phys., 14, 265 (1942).

29. R. H. Wiswall and C. P. Smyth, J. Chem. Phys., 9, 356 (1941).

30. W. C. Price, Chem. Revs., 41, 257 (1947).

31. L. C. Jones and L. W. Taylor, Anal. Chem., 27, 228 (1955).

32. J. T. Gary and L. W. Pickett, J. Chem. Phys., 22, 599 (1954).

33. J. T. Gary and L. W. Pickett, J. Chem. Phys., 22, 1266 (1954).

34. D. Semenow, A. J. Harrison and E. P. Carr, J. Chem. Phys., 22, 638 (1954).

35. F. O. Rice, J. Am. Chem. Soc., 42, 727 (1920).

36. F. A. Matsen, W. W. Robertson, and R. L. Chuoke, Chem. Revs., 41, 273 (1947).

37. H. P. Koch, J. Chem. Soc., 387 (1949).

38. E. P. Kohler and H. Potter, J. Am. Chem. Soc., 57, 1316 (1935).

39. H. P. Koch, J. Chem. Soc., 408 (1949).

40. E. A. Fehnel and M. Carmack, J. Am. Chem. Soc., 71, 231 (1949).

41. E. A. Fehnel and M. Carmack, J. Am. Chem. Soc., 71, 84 (1949).

42. H. H. Jaffe and L. D. Freedman, J. Am. Chem. Soc., 74, 1069 (1952).

43. C. Eaborn, Organosilicon Compounds, Academic Press, Inc., New York, N. Y., 1960.

44. H. Gilman and G. E. Dunn, J. Am. Chem. Soc., 72, 2178 (1950).

45. W. G. Woods, R. A. Carboni, and J. D. Roberts, J. Am. Chem. Soc., 78, 5653 (1956).

46. A. Streitwieser, Molecular Orbital Theory, J. Wiley and Sons, Inc., New York, N. Y., 1961.

47. R. E. Ireland and P. W. Schiess, J. Org. Chem., 28, 6 (1963).

48. H. Labhart and G. Wagniere, Helv. Chim. Acta, 42, 2219 (1959).

49. A. D. Petrov and V. F. Mironov, Doklady Akad. Nauk S.S.S.R., 80, 761 (1961); Chem. Abstr., 46, 11102a (1952).

50. W. I. Kaye, Appl. Spectroscopy, 15, 130 (1961).

51. C. C. Price and S. Oae, Sulfur Bonding, Ronald Press Co., New York N. Y., 1962.

52. C. S. Marvel and J. K. Stille, J. Am. Chem. Soc., 80, 1742 (1958).

53. K. C. Brannock, J. Am. Chem. Soc., 81, 3379 (1959).

54. R. H. Saunders, U. S. Patent 2,501,144; March 21, 1950.

55. A. D. Petrov and E. A. Chernyshev, Doklady Akad. Nauk S.S.S.R., 67, 1045 (1949).

56. A. D. Petrov, M. A. Cheltsova and E. A. Chernyshev, Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 1087 (1952); Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 949 (1952).

57. D. Seyferth and M. A. Weiner, J. Am. Chem. Soc., 83, 3583 (1961).

58. D. Seyferth and M. A. Weiner, J. Org. Chem., 26, 4797 (1961).

59. C. E. Castro and W. C. Kray, J. Am. Chem. Soc., 85, 2768 (1963).

60. H. Schmidt and P. Karrer, Helv. Chim. Acta, 32, 1371 (1949).

61. E. J. Corey and H. Uda, J. Am. Chem. Soc., 85, 1788 (1963).

62. J. E. Johnson, R. H. Blizzard and H. W. Carhart, J. Am. Chem. Soc., 70, 3664 (1948).

63. L. Friedman, Abstracts from 122nd Meeting of the American Chemical Society, Atlantic City, Sept. 1952, p. 46-M.

64. Huang-Minlon, J. Am. Chem. Soc., 68, 2487 (1946).

65. E. L. Eliel, Stereochemistry of Carbon Compounds, McGraw-Hill Co., New York, N. Y., 1962, p. 188.

66. P. D. Bartlett, Ann., 653, 52 (1962).

67. N. D. Field, J. Org. Chem., 25, 1006 (1960).

68. D. Mikulasova and A. Hrivik, Chem. zvesti, 11, 641 (1957); Chem. Abstr., 52, 9028b (1958).

69. A. Hrivik and D. Mikulasova, Chem. zvesti, 12, 32 (1958); Chem. Abstr., 52, 13616b (1958).

70. R. W. Stackman, Ph. D. Dissertation, University of Florida, January, 1961.

71. S. D. Rosenberg, J. J. Walburn, T. D. Stankovich, A. E. Balint, and H. E. Ramsden, J. Org. Chem., 22, 1200 (1957).

72. A. D. Petrov and V. F. Mironov, Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 635 (1952); Chem. Abstr., 47, 10471i (1953).

73. N. S. Nametkin, A. V. Topchiev, S. G. Durgaryan, and N. A. Kuzmina, Zhur. Obschei Khim., 30, 2594 (1960); Chem. Abstr., 55, 14345h (1961).

74. H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, J. Am. Chem. Soc., 71, 1499 (1949).

75. R. Ciola and R. L. Burwell, J. Org. Chem., 23, 1063 (1958).

76. A. T. Babayan, M. G. Indzhikyan, and L. R. Tumanyan, Dokl. Akad. Nauk Arm. S.S.S.R., 36 (2), 95 (1963); Chem. Abstr., 59, 6281f (1963).

77. P. D. Bartlett, W. D. Closson, and T. J. Codgell, J. Am. Chem. Soc., 87, 1308 (1965).

APPENDIX

HMO Δm CALCULATIONS ($k_{___} = 0.6\beta$)

Pseudo-butadiene

$\overset{1}{C}—\overset{2}{C}---C—C$

Symmetrical operation:

$$\begin{vmatrix} x & 1 \\ 1 & x + 0.6 \end{vmatrix} = 0$$

$$x^2 + 0.6x - 1 = 0$$

$$x = \frac{-0.6 \pm \sqrt{0.36 + 4}}{2} = \frac{-0.6 \pm 2.09}{2} = \begin{cases} -\frac{2.69}{2} = -1.345 \\ \frac{1.49}{2} = 0.745 \end{cases}$$

$x = \pm 1.345, \pm 0.745$ (even alternant hydrocarbon)

$\Delta m = 2 \times 0.74 = 1.49$

Pseudo-hexatriene

$\overset{1}{C}—\overset{2}{C}---\overset{3}{C}—C---C—C$

Symmetrical operation:

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 0.6 \\ 0 & 0.6 & x+1 \end{vmatrix} = 0.$$

$$x \begin{vmatrix} x & 0.6 \\ 0.6 & x+1 \end{vmatrix} - \begin{vmatrix} 1 & 0.6 \\ 0 & x+1 \end{vmatrix} = 0$$

$x(x^2 + x-0.36) - (x + 1) = 0$

$x^3 + x^2 -0.36\ x-x-1 = 0$

$x^3 + x^2 -1.36\ x-1 = 0$

Solution by substitution and synthetic division:

1	+1	-1.36	-1	1.09
	1.09	2.28	1.002	
1	2.09	0.92		

$x^2 + 2.09\ x + 0.92 = 0$

$$x = \frac{-2.09 \pm \sqrt{4.37-3.68}}{2} = \frac{-2.09 \pm \sqrt{0.69}}{2} = \frac{-2.09 \pm 0.83}{2} = \begin{cases} -\frac{1.26}{2} = -0.63 \\ -\frac{2.92}{2} = -1.46 \end{cases}$$

$x = \pm 1.46, \pm 1.09, \pm 0.63$ (even alternant hydrocarbon)

$\Delta m = 2 \times 0.63 = 1.26$

Pseudo-octatetraene

1 2 3 4
C—C---C—C---C—C---C—C

Symmetrical operation:

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 0.6 & 0 \\ 0 & 0.6 & x & 1 \\ 0 & 0 & 1 & x+0.6 \end{vmatrix} = 0$$

$$x \begin{vmatrix} x & 0.6 & 0 \\ 0.6 & x & 1 \\ 0 & 1 & x+0.6 \end{vmatrix} - \begin{vmatrix} 1 & 0.6 & 0 \\ 0 & x & 1 \\ 0 & 1 & x+0.6 \end{vmatrix}$$

$$x^2\begin{vmatrix} x & 1 \\ 1 & x+0.6 \end{vmatrix} - 0.6x\begin{vmatrix} 0.6 & 1 \\ 0 & x+0.6 \end{vmatrix} - \begin{vmatrix} x & 1 \\ 1 & x+0.6 \end{vmatrix}$$

$x^2(x^2 + 0.6x-1) -0.6x (0.6x + 0.36) - (x^2 + 0.6x-1)$

$x^4 + 0.6x^3-x^2-0.36x^2-0.216x-x^2-0.6x + 1$

$x^4 + 0.6x^3-2.36x^2-0.816x + 1$

Solution by substitution and synthetic division:

1	+0.60	-2.360	-0.817	+1	-0.92
	-0.92	0.294	1.900	-1	
1	-0.32	-2.066	1.084		

$x^3-0.32x^2-2.066x + 1.084 = 0$

Solution by substitution and synthetic division:

1	-0.32	-2.066	+1.084	1.27
	1.27	1.208	-1.089	
1	0.95	-0.858		

$x^2 + 0.95x - 0.858 = 0$

$$x = \frac{-0.95 \pm \sqrt{0.903 + 3.43}}{2} = \frac{-0.95 \pm \sqrt{4.333}}{2} = \frac{-0.95 \pm 2.08}{2} = \begin{cases} \frac{-3.03}{2} = -1,515 \\ \frac{1.13}{2} = 0.565 \end{cases}$$

$x = \pm 1.515, \pm 1.27, \pm 0.92, \pm 0.565$ (even alternant hydrocarbon)

$\Delta m = 2 \times 0.565 = 1.13$

BIOGRAPHICAL SKETCH

Bruno Iachia was born on November 23, 1933, in Milan, Italy. He attended elementary and secondary schools in Milan, Italy, and graduated from Liceo Beccaria in 1951. The author attended the University of Pavia, Italy, from November, 1951 to October, 1956, when he received the degree of Doctor in Pharmacy.

He entered the Graduate School at the University of Toronto, Canada, in September, 1957, and received the degree of Master of Arts with major in Chemistry in November, 1959. After working two years as research chemist for Canadian Industries, Ltd., he enrolled in the Fall of 1961 in the Graduate School at the University of Florida. While pursuing his work toward the degree of Doctor of Philosophy, he held two summer positions as research chemist for General Motors (Technical Center), in 1962, and for Atlantic Refining Company (Research Laboratories), in 1963.

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August, 1966

Dean, College of Arts and Sciences

Dean, Graduate School

Supervisory Committee:

Chairman